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ADDITIONAL EVIDENCE AS TO THE INTERCELLULAR FORMATION OF CONNECTIVE TISSUE

By George A. Baitsell

Osborn Zoölogical Laboratory, Yale University

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In a previous communication[1] to the Academy, evidence was presented to show that the connective tissues in the amphibian embryo arise by the direct transformation of an intercellular secretion rather than by a modification of embryonic cytoplasm. Thus, the process is fundamentally intercellular, rather than intracellular. It was also shown in this communication that the intercellular secretion, which constitutes the ground substance of the connective tissues, was of such a nature that, under the influence of various factors—probably both chemical and mechanical in character—it gives rise to the characteristic connective tissue fibers by means of a gradual consolidation and fusion of the minute structural elements of which it is composed. This gradual transformation of the more or less homogeneous, secreted ground substance into a definite fibrous tissue appears, from the morphological standpoint at least, to be identical with that which takes place, under certain conditions, in the transformation of the fibrin of a blood clot into a fibrous tissue, as shown by previous experiments.[2]

Since that time, Harrison,[3] in his investigations on the development of the balancer in Amblystoma, has reached the same conclusion with regard to the formation of connective tissue in this group. He says: "The balancer membrane thus affords a clear proof that connective tissue fibers take origin in an amorphous ground substance, independently of any direct action on the part of the mesenchyme cells." Furthermore, the results from studies[4] on the development of connective tissue in the chick embryo show that essentially the same process obtains there.

For some time investigations have been in progress, under a grant from the National Tuberculosis Association (Medical Research Committee), in an endeavor to determine the origin of the fibrous tissue which, as a rule, forms so abundantly in regions infected with tubercle bacilli, and which undoubtedly plays a very important rôle in the control of the in-

fection and the healing of the affected tissues. Thus it has recently been stated[5] that "The importance of fibrosis in the healing or partial healing of a tubercle cannot be over-estimated. As the connective tissue cells lay down more and more collagen in their peripheries, the intercellular tissue spaces are encroached upon and finally closed, thereby obliterating the only channels of communication between the interior of the lesion and the surrounding tissues. Tubercle bacilli and their soluble products can no longer readily escape from the focus of infection; extension of the infection can no longer take place, and absorption of tuberculin-like bodies can no longer poison the system." It is evident from the above that the question of fibrosis in tuberculosis is a very important one. It is believed that the results herewith presented give clear evidence as to the method of formation of this material in experimentally infected testicular tissues of the guinea pig.

In the present studies[6] on the development of fibrous tissues in tubercular infections, the testes of guinea pigs have been used. The selection of the testis, which has proved to be an almost ideal field for these investigations, was made after an extensive examination of various other organs and tissues. Long[7] had already shown that the testis afforded a very favorable field for his studies on tuberculin. He found that the extent of the degenerative processes, following an injection of tuberculin into the testis, could be used as a direct indicator of the strength of the tuberculin solution. Long also studied the response of the testicular tissues to the living tubercle bacilli and noted that, along with other striking degenerative changes, an abundant formation of fibrous tissue occurred; thus giving evidence that these tissues were adapted for use in the present studies. The exposed position of the testis, making the direct inoculation of any desired region easy; their paired condition, giving a control testis for comparison; and, finally, their unique histological structure, which readily permits following and interpreting the degenerative structural changes that take place, are additional advantages which have been found to be of great importance for these experiments.

Following the general plan used by Long, pairs of male guinea pigs were chosen—the members of each pair being of approximately equal weight. One from each pair, which was termed the reinfected animal, received two inoculations of living tubercle bacilli; the first being a sensitizing inoculation, usually intraperitoneal in which bacilli of low virulence were used; the second, given three weeks later, being a direct inoculation into one testis, of a suspension of highly virulent bacilli. The other animal of each pair, which was termed the control animal, received only the direct testicular inoculation. The response of the testicular tissues in the reinfected animals to the direct inoculation is much more rapid and severe than in the control animals. Later, however, as the infection progresses,

the histological picture in the testes of the two types is apparently identical.

The study of sections shows that the inoculation of living tubercle bacilli into the testis results very shortly in an almost complete degeneration and elimination of the germinal cells from the seminiferous tubules, so that the latter are soon emptied and appear shrunken. Coincident with these changes in the tubules, an abundant exudate appears in the intertubular areas of the testis. In well-preserved material, it is clear that the seminiferous tubules lie, for the most part, in quite close contact so that the intertubular areas are normally quite small, but they soon become greatly enlarged; due, apparently, to the shrinkage of the tubules and the presence of the exudate. Along with the exudate in the intertubular areas varying degrees of cellular infiltration may occur. In many cases, however, large areas of the exudate are practically cell free when first observed.

We may now turn our attention to the origin of the fibrous tissue which, as a rule, is formed so abundantly that within a few weeks after the inoculation, the histological picture of the testis is almost completely changed, the germinal tissues being largely replaced by masses of fibrous tissue. What has been the method of formation? It may be said that the present studies on the infected testicular tissues give clear evidence that the process of fibrosis results from a direct transformation of the exudate present in the intertubular areas. The permanent preparations present a striking and consistent series which is easily interpreted on this basis.

The exudate when first noted appears, for the most part, quite homogeneous or with a fine fibrillation. The later stages show gradual stages in the direct transformation of this material into a typical fibrous tissue, together with the formation of heavy bundles of wavy fibers which stain very beautifully and typically with a Mallory stain. This fibrous tissue encapsulates and infiltrates the tubercles which have been forming in the infected areas, and usually develops in such great abundance throughout the infected areas, as noted above, that the testicular tissues are largely transformed into fibrous tissue.

The transformation of the exudate is not dependent upon direct cellular connections, and is seen to best advantage in intertubular areas in which cells are few in number or entirely lacking. From the morphological standpoint, at least, the process which results in the formation of fibrous tissue from the exudate in the intertubular areas of a testis infected with tubercle bacilli appears to be identical with that which takes place in the development of connective tissue in the embryos of the frog and the chick, and in wound healing in the skin of the adult frog.

Thus it seems safe to conclude from the several lines of evidence now at hand that connective tissue formation is essentially an intercellular

process in which certain cell secretions undergo a direct morphological transformation by a process apparently of the same character as that which takes place in the transformation of a plasma clot.

[1] Baitsell, G. A., *Proc. Nat. Acad. Sci.*, **6**, 1920, p. 77; *Amer. J. Anat.*, **28**, 1921, p. 431.

[2] Baitsell, G. A., *J. Exp. Med.*, **21**, 1915, p. 455; *Ibid.*, **23**, 1916, p. 739; *Amer. J. Physiol.*, **44**, 1917, p. 109.

[3] Harrison, R. G., *J. Exp. Zoöl.*, **41**, 1925, p. 412.

[4] Baitsell, G. A., *Quart. J. Micr. Sci.*, **69**, 1925, p. 571.

[5] Baldwin, Petroff & Gardner, *Tuberculosis, etc.*, Lea & Febiger, Philadelphia; 1927, p. 104.

[6] A preliminary report of these studies was presented at the 22nd annual meeting of the National Tuberculosis Assoc., Washington, D. C., Oct., 1926.

[7] Long, E. R., *Amer. Rev. Tuber.*, **9**, 1924, p. 215; Smith, M. I., *Jour. Med. Res.*, **43**, 1922, p. 45.

RESULTS OF HETEROPLASTIC TRANSPLANTATIONS OF THE HEART RUDIMENT IN AMBLYSTOMA EMBRYOS

BY W. M. COPENHAVER

DEPARTMENT OF ANATOMY, UNIVERSITY OF ROCHESTER, AND OSBORN ZOÖLOGICAL LABORATORY, YALE UNIVERSITY

Communicated May 21, 1927

Adults of the two species of salamanders, *Amblystoma punctatum Linn.* and *Amblystoma tigrinum Green*, differ considerably in size, adult tigrinum salamanders reaching a length of about 25 cm. (in extreme cases 32 cm.) while adult punctatum individuals measure about 16 cm. in length. However, early embryos of the two species are of approximately the same size; at the time of complete yolk resorption the tigrinum embryos may even be smaller than those of punctatum. These two species, therefore, provide suitable material for transplanting an organ rudiment which at the time of operation and during early larval life is of a similar size in the two species but which becomes markedly different in magnitude in later development.

Transplantations of the fore-limb rudiment between the two species have been described by Harrison,[1] who has found that a tigrinum limb transplanted to a punctatum embryo grows much more rapidly than it would have grown if left in place, and that even after ten or twelve weeks, when the tigrinum larva is much larger than the punctatum of corresponding age, the grafted limb is larger than the control limb of either species. On the other hand, the fore limb of punctatum grafted to a tigrinum embryo, although getting an initial start ahead of its normal tigrinum

control, nevertheless ultimately remains very much smaller, and for a long time is smaller than the control limb of the punctatum donor even though the latter is a much smaller animal.

To account for these unexpected results Harrison suggests that in addition to ordinary nutritional factors, two other important factors must be assumed to play a part. First, there exists within the organ itself a factor determining the size to which the organ may ultimately grow; this is greater in A. tigrinum. Second, controlling the rate of growth of the organs of the embryo, there is in the circulating medium a growth regulator; this is apparently greater in A. punctatum. Whatever this regulator of growth rate may be, it seems quite likely that it is in some way associated with energy utilization, of which metabolic rate may serve as an index. This idea has been expressed by Harrison and it is also known from determinations made by Helff[2] that the metabolic rate in punctatum embryos is considerably higher than in embryos of A. tigrinum.

The experiments here reported were done for the purpose of testing these growth relations in an organ particularly vital to the embryo. The experiments also afford an opportunity for studying pulsation rates in hearts exposed to a foreign environment, such as the innervation and blood supply of a different species.

The heart transplantations were done in the usual way at the tail bud stage of development (stage 29),[3] during the period when the heart rudiment consists of lateral folds of mesoderm and a small group of medially placed cells representing the endocardial anlage. This is earlier than the first pulsations and considerably before the time when the nerve supply reaches the heart.

The mortality after such operations is high, but a total of twenty-eight punctatum embryos with hearts grafted from A. tigrinum have been kept alive beyond the stage when the circulation is established and nine have been kept until the beginning of metamorphosis. In all cases acceleration of growth rate began to appear early, a difference in size being evident by the time of complete yolk resorption. The contrast in size gradually became more marked and by sixty days after the operation the grafted heart, compared as to total bulk, was about twice the size of the heart of control punctatum embryos. In general, therefore, the results agree with the results of limb transplants, but by the time of metamorphosis the ratio of size of the transplanted heart to the control punctatum heart was less than at the sixty-day period. Apparently functional regulation had served to bring the organ nearer to the size normal for the host species.

In the reciprocal experiment, involving transplantations of the heart from A. punctatum to A. tigrinum, the transplanted organ grew more slowly than the normal. This result is also similar to the results of limb transplants. In the case of the heart, however, the organ was clearly insufficient

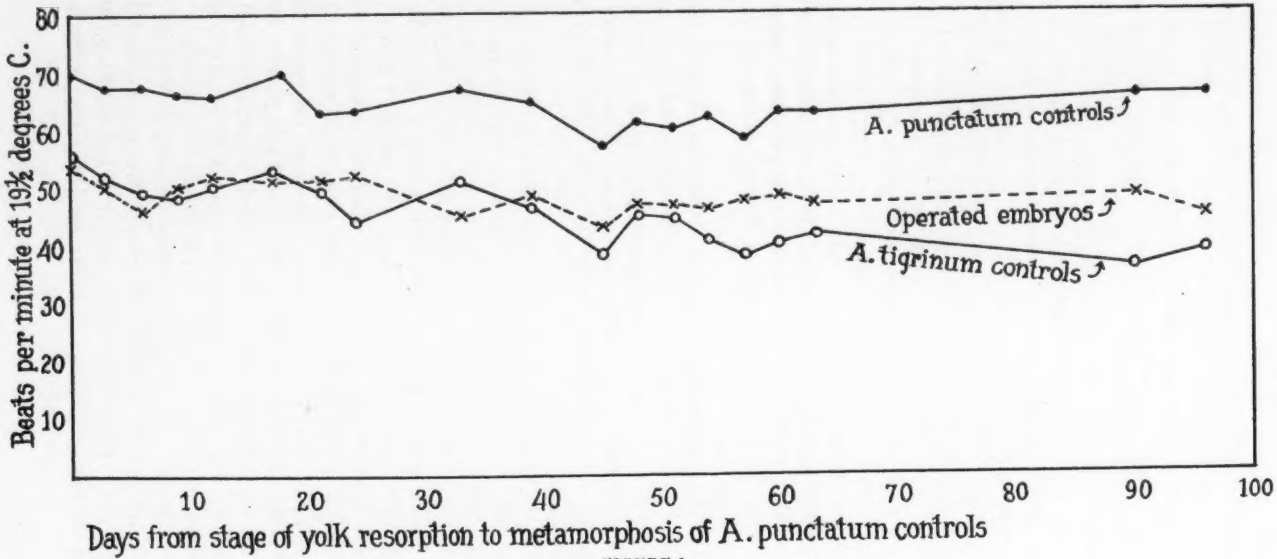
Beats per minute at 19½ degrees C.
80
70
60
50
40
30
20
10
A. punctatum controls
Operated embryos
A. tigrinum controls
10
20
30
40
50
60
70
80
90
100
Days from stage of yolk resorption to metamorphosis of A. punctatum controls

FIGURE 1

for normal function and the embryos became œdematous and lived for only a few weeks.

In addition to transplantations of the organ rudiment as a whole, a few experiments were made in which the posterior half of the heart was removed from a tigrinum embryo and replaced by approximately the posterior half (rudiment of sinus and atrium) from a punctatum embryo. Only four operations of this type were successful, but in these the results were clearly different from the results of transplantation of the organ as a whole from A. punctatum to A. tigrinum. After transplantation of a half, the organ, especially the posterior part, was smaller than normal but was large enough to function during the whole embryonic period, two of the four embryos being kept alive until beginning of metamorphosis.

Pulsation rates have been counted in all heteroplastic graft experiments and these have been compared with pulse rates of animals subjected to control operations (homoplastic grafts) and normal unoperated controls. The normal rate of A. punctatum is considerably higher than that of A. tigrinum, a fact which is interesting in view of the metabolic rate determinations already referred to.

The figure gives a comparison of averages for controls and operated embryos (A. punctatum with heart transplanted from A. tigrinum). The average includes only the records for the nine operated embryos which lived until beginning of metamorphosis. It is evident that the rate for operated embryos is much nearer the rate of the donor than to that of the host species. Apparently the heart of Amblystoma embryos possesses within itself not only the capacity for rhythmical pulsation but also a factor for the rate, and tends to maintain that rate approximately, when placed in a new environment such as the embryo of another species.

Rates in the reciprocal experiments (transplantations of the entire organ from A. punctatum to A. tigrinum) are not given, since the abnormally small heart produced by this cross brought about an œdematous condition of the host. However, a half transplant from A. punctatum to A. tigrinum was sufficient for normal life of the embryo, and the rates in this series were higher than the rates normal for the host species but in the few studied did not approximate the rate of the donor species to as great degree as in experiments of the type illustrated in figure 1. The two series, however, are transplants in the opposite direction and thus far the results do not justify the conclusion that a transplant of the whole of the heart (sinus, atrium, ventricle, and bulbus) approximates the donor rate more nearly than a transplant of posterior half alone, that is, sinus and atrium.

Since the transplantations were made before the time when the nerve supply grows into the heart, the nerves to the transplanted organ must have come from the host system. These nerves are apparently functional in the grafted organ, according to drug experiments made on some of the

embryos. It was found that small quantities of atropine injected through the body wall and over the pericardium had little or no effect on the heart rate. On the other hand, small quantities of pilocarpine definitely slowed the rate and the rate could be brought back approximately to normal by injecting atropine. These results were similar for control and operated embryos. Thus the heart muscle retains approximately its specific rhythm, even though it is under control of the nervous system of a species having a different rhythm.

[1] Harrison, R. G., *Proc. Nat. Acad. Sci.*, 1924, **10**, 69.
[2] Helff, O. M., *Anat. Rec.*, 1926, **34**, 128.
[3] Copenhaver, W. M., *J. Exp. Zoöl.*, **43**, 321.

VISION AND RETINAL STRUCTURE IN MICE

BY A. E. HOPKINS*

ZOÖLOGICAL INSTITUTE OF THE UNIVERSITY OF MUNICH, GERMANY

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According to Schultze (1866), Detwiler (1924) and others, the retina of the mouse is of the all-rod type. Krause (1895), however, succeeded in finding a few cones among the numerous rods present. If the duplicity theory holds, it is to be expected that mice are either color blind or have only a very poorly developed color sense, according to whether few or no cones are present in the retinae. With the purpose of testing the duplicity theory, by use of mice, the following experiments were begun.

To Professor K. von Frisch I owe thanks for suggesting this work to me and for his stimulating criticism and advice.

The experimental apparatus consisted essentially of an open box with two outlets, one through colored and one through white, black or gray Hering papers. By means of electrical punishment plates in the two outlets the animals were trained to choose the door through one of the papers as required. The papers were interchanged in position in an irregular manner. In the initial training either white or black was employed opposite the color, depending upon which would be expected to differ most markedly from the color when seen by a color-blind animal. By using different members of the Hering 50-step gray series the intensity of the non-colored paper was varied in the attempt to find a gray which the specimens could not distinguish from the color.

Four mice were so tested for color vision, three with red and one with blue papers. The last was unable to distinguish between blue and gray no. 13, which is among the lighter members of the gray series, although he

discriminated between blue and other grays both lighter and darker than this. Two of the specimens tested for red vision similarly confused the red paper with the very dark gray no. 49. The other mouse gave uncertain results but apparently he could not distinguish between red and a dark gray which was between numbers 49 and 50 in brightness.

The employment of colored papers for experiments of this kind has certain disadvantages for physiological purposes. In order to obtain results of a more conclusive nature an apparatus was assembled which would throw two beams of light, one colored and one neutral, into the experiment box so as to fall upon a single piece of cardboard in the position previously occupied by the Hering papers and with similarly placed doors. Properly adjusted diaphragms made the beams of the size required to produce two fields of light, alike in size and shape, on the cardboard. The apparatus could be altered to interchange the two fields in position. That the method is satisfactory is evident from the fact that mice, given initial training with Hering papers, would continue choosing correctly when transferred to dark room conditions where similar combinations of colored and neutral light-fields obtained. A prism in the color-producing apparatus separated the light of this beam into its components and the rays of desired wave-length were carefully selected. The wave-lengths employed were: red, 610–750$\mu\mu$; green, 490–550$\mu\mu$; and blue, 455–490$\mu\mu$. Photographic plates, exposed for different lengths of time and arranged in series, were placed in the neutral beam to vary the brightness of the non-colored light field.

With this apparatus, and under dark room conditions, four mice were demonstrated to be color blind, for the colors employed, while one specimen was apparently able to see red as a color. Two animals were unable to discriminate between green and the field of neutral light of intensity 27.2 meter candles. One specimen completely confused the blue with neutral light of intensity 2.1 m.c., and one mouse was equally unable to distinguish between the red and the non-colored field of intensity 0.04 m.c. The other specimen, however, distinguished between red and each of a great number of neutral intensities and showed certain other significant differences from the mice already described in mode of choice. It was shown that his ability to discriminate between two neutral light fields of different intensities was not as fine as would be required to explain the results on the basis of brightness discrimination. This was the same specimen which had given uncertain results in the tests with Hering papers. The conclusion appears to be justified that this specimen could actually see the color red as a quality.

Microscopic examination of preparations of the retinae of the experimental mice, and of many others, has failed to reveal the presence of structurally differentiated cones among the rods. The results from the

color-blind specimens agree well with the observed structure, according to the duplicity theory. Conclusive observations on the retinae of the color-seeing specimen could not be made for these retinae are abnormal in that all elements appear to be under-developed. In thickness this type of retina is only about one-fourth of the normal and the component structures are correspondingly small. It is thought possible that some cones may be present, but in such an incompletely differentiated state as not to permit identification.

On sectioning the eyes of the experimental mice it was found that one of them, which had given excellent evidence of seeing but which was color blind for green, had retinae of a type similar to that described by Keeler (1927), in which the external nuclear and rod layers are not differentiated. Rods, clearly developed ones at least, could not be found, and the retina probably represents a condition of checked development. While Keeler stated that his mice were blind, the above-mentioned specimen and one other were quite clearly able to see or else they had made choices on the basis of some factor entirely overlooked by the experimenter, although all probable sources of error had been controlled.

It was, therefore, desirable to find other specimens with such retinae and to determine with certainty if they could see. To this end, one eye was removed from each of many mice and sectioned. Keeler had noted that the two eyes of a specimen are alike and the author also found this to be true. The animals having "rodless" eyes were then trained in the usual manner to choose white opposite red Hering paper. The specimens learned as readily as could be expected of mice recently deprived of one eye. Five animals were carried through series of tests which proved that they could see.

After they had learned to choose the white paper opposite red, these two papers were exchanged for green and black ones, as an odor control, and all chose green, the lighter. After the initial training most of the tests were made without current in the electric punishment plates to prevent the animals learning to feel the current with their vibrissae, as Keeler stated was the case. Then tests were made under dark-room conditions with the above-described apparatus, and the animals still chose white.

The only known factor that had not been controlled was the experimenter and it was thought to be very remotely possible that the observer unconsciously influenced the choices of the animals. Therefore, it was arranged for Professor von Frisch to make tests, in the absence of the author, under dark-room conditions, with one of the mice, having one abnormal eye, which had previously been trained only with Hering papers. This was done and the specimen chose the white field and avoided the red one with such a degree of correctness as to leave no place for reasonable doubt as to the animal's ability to see.

After the tests with these one-eyed mice were completed their eyes were removed and fixed, and tests continued with the blinded specimens to see if they could learn to choose on some basis other than vision. In long series of tests they showed no ability to choose properly. These results are considered to be adequate proof that the specimens could see.

Structurally this type of retina represents a semi-embryonic condition. The layer of cells which normally gives rise to the internal and external nuclear layers, the latter of which contains the nuclei of the rods, remain as a single layer. No structures have been found which can definitely be identified as rods.

In order to get some concept of how eyes of this type can function in vision it is necesssry to think of rods in the physiological, rather than in the morphological sense. It seems to be unknown at just what stage of embryonic development the retina becomes functional, but it is conceivable that function may begin before the rods and cones have become structurally differentiated. It may be said that, in the present case, the potential rod cells are present and although they are morphologically in such a state as not to be readily recognizable, they are internally or physiologically well enough differentiated to function.

Several different methods were employed in the effort to find visual purple in these retinae, but without success. If visual purple is present it is in such small quantity as to escape observation.

It was found that one mouse could see color, although no cones could be identified in the retinae, and that a number of specimens could see, on the basis of brightness, in spite of the fact that the retinae contained no clearly differentiated rods. The results are not considered to be in opposition to the duplicity theory, for it was found that in most cases mice with normal retinae were color blind. Since retinae containing very incompletely differentiated rod cells may function as light sensitive organs it is equally possible that in some cases functional cones may be so poorly developed structurally as not to be recognizable. Although in the retinae examined histologically no cones were found, the success of Krause (1895) in identifying cones in the mouse retina indicates that some mice at least may possess cones. With the assumption that this was the case for the color-perceiving mouse, with the qualification in regard to the degree of structural differentiation, the present results constitute a support of the duplicity theory.

A complete account of this work will be published in an early number of the *Zeitschrift für vergleichende Physiologie.*

* Parker Traveling Fellow from Harvard University.

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ZEEMAN EFFECT AND STRUCTURE IN THE SPARK SPECTRA OF TIN

(Preliminary Report)

BY J. B. GREEN* AND R. A. LORING

JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY

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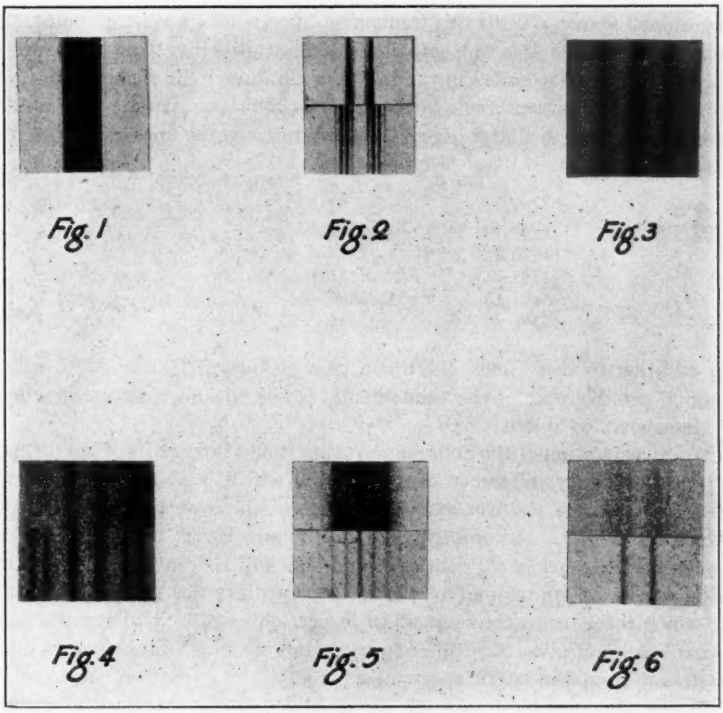
In a previous communication (these PROCEEDINGS, **13**, p. 347, May, 1927) the authors described a method by which it was possible to resolve some of the hitherto unresolved Zeeman patterns of tin. The region between 4500 A.U. and 6000 A.U. in the spectrum is very rich in spark lines and there is only one strong arc line in this neighborhood, λ 5631. The source used, a type of vacuum arc, was found to produce the spark lines in this region with considerable intensity, and several of the patterns could be resolved and the terms involved determined in this way.

The patterns were found to be of two kinds; those arising from combinations between doublet terms, and those arising from combinations between triplet terms or between triplet and singlet terms. These two types of lines are evidently of the spectra of the singly ionized and doubly ionized tin. Other evidence in support of this view is given by Kimura and Nakamura[1,2] and Kimura[3] who studied several metallic spectra under different conditions of excitation and were able to classify the spark lines of tin into three groups, corresponding to Sn^{+}, Sn^{++} and Sn^{+++}. The authors' classification of lines into spectra of successively ionized tin agree with those of Kimura and Nakamura in all but a very few cases.

Back[4] in a study of the Zeeman effect in lead found two lines, one in the red and one in the yellow, λλ 6660 and 5608, whose patterns were identical with those of the D lines, and he consequently assigned them to the principal series of the spectrum of ionized lead. The frequency difference between these lines is 2813 and this number gave a clue to Gieseler[5] who has succeeded in working out the spectrum of Pb^{+} although only this pair of lines has been checked by its Zeeman pattern.

A pair of Sn lines, both in the red, λλ 6844 and 6453, and having a frequency difference of 884 were observed on the plates measured in our earlier paper and 6453 was found to have the same pattern as the lead line λ 5608



Description of Plate.

FIGURE 1

Sn arc 3801, second order. (0) (0.34) 0.72 1.07 1.40

FIGURE 2

Sn arc 3330, second order. Upper, parallel components; lower, perpendicular components. (0.47) (0.90) 0.63 1.05 1.48 1.93.

FIGURE 3

Sn arc 3009, fourth order. (0.11) 1.43. Outside component resolved on plate, but not measurable on account of plate grain.

FIGURE 4

Upper, Sn^{++} 4858, second order. } $^3S_1{}^3P_1$
Lower, Zn 4722, second order. }

FIGURE 5

Upper, Sn^{++} 4586, second order. } $^3S_1{}^3P_2$
Lower, Zn 4810, second order. }

FIGURE 6

Sn^{+} 5597, first order. New line. Upper, perpendicular components; lower, parallel components.

About twelve times enlarged. Second order scale about 0.96 A.U. per mm. on original plates.

mentioned above. With this frequency difference as a starting point, the authors have been able to locate a diffuse multiplet, involving a line which has not yet been recorded in the tables of tin lines. Since then, considerable progress has been made in the analysis of the spectrum. The results will be published in a later paper. Below are given the lines in their multiplet arrangement.

	$^2S_1$	$^2D_2$		$^2D_3$
$^2P_1$	6843.81	5332.91		
	14607.7	*18746.3*		
	(*883.8*)	(*883.6*)		
$^2P_2$	6453.15	5596.69	(*108.9*)	5562.74
	15491.5	*17862.7*		*17971.8*

In addition to these lines, there is a pair of lines, 5799 and 5590, which form a possible pair of the fundamental series, although this assignment is somewhat in doubt.

An investigation of the Schumann region shows three pairs of strong lines with a frequency difference of about 4250 which is about the value we should expect for the frequency difference of the lowest ^2P terms of the spectrum of Sn^+. According to Goudsmit and Back[6] the difference between the averages of s^3P_0 and s^3P_1 and s^3P_2 and s^1P_1 in the arc spectrum should give us approximately the frequency difference of the two levels to which these terms converge. An inspection of table 1 of the previous communication gives this difference as 4166, a value quite close to 4250 as found from the spark spectrum.

It was also possible to arrange several lines of the spectrum of doubly ionized tin into a $^3P^3D$ multiplet and a $^3P^3S$ multiplet. These assignments are shown below.

	$^3S_1$	$^3D_1$		$^3D_2$		$^3D_3$
$^3P_0$	4924.12	5369.3				
	20302.5	18619				
	(*275.9*)	(*276*)				
$^3P_1$	4858.12	5291	(*205.2*)	5349.18		
	20578.4	*18895*		*18689.8*		
	(*1222.8*)	[*1223*]		(*1223.2*)		
$^3P_2$	4585.62	4969.2	[205]	5020.5	(*312.1*)	5100.38
	21801.2	*20118*		*19913*		*19600.9*

The ratio of $^3P_2 - {}^3P_1$ to $^3P_1 - {}^3P_0$ should be 2:1, and it is found to be about 4:1, while that of $^3D_3 - {}^3D_2$ to $^3D_2 - {}^3D_1$, which should be 3:2 is found to be very close to the theoretical value.

One line, λ4330, appeared on the plates as an intercombination between a $^3S_1$ and a $^1P_1$ term. Another line, 4618, appears to be a $^3P_0{}^3S_1$ combination.

There are four other lines, 3765, 3860, 3963, 4216, which have Zeeman

effects like those due to combinations between ^2P and ^2S terms. These lines are very likely due to trebly ionized tin.

NO.	WAVE LENGTH	ZEEMAN EFFECT						TYPE
1	6844	(Not observed)						$^2S_1{}^2P_1$
		(0.67)	1.33	(calc.)				
2	6453	(0.36)	**1.01**	1.66	(obs.)			$^2S_1{}^2P_2$
		(0.33)	**1.00**	1.66	(calc.)			
3	5799	1.07	(0)	0.96				$^2D_3{}^2F_{3,4}$?
4	5596	(...)	**(0.80)**	**0.55**	**1.06**	1.60		$^2P_2{}^2D_2$
		(0.37)	**(0.80)**	**0.53**	1.07	1.60		
5	5589	(0)	0.90					$^2D_2{}^2F_2$?
6	5562	(0)		1.04				$^2P_2{}^2D_3$
		(0.07)	(0.20)	**1.00**	1.13	1.27	1.40	
7	5369	(0)	0.48					$^3P_0{}^3D_1$
		(0)	0.50					
8	5349	(0)		0.96				$^3P_1{}^3D_2$
		(0)	(0.33)	**0.83**	1.17	1.50		
9	5333	(0)		0.835				$^2P_1{}^2D_2$
		(0.07)	0.73	0.87				
10	5291	(0.95)	0.47	1.41				$^3P_1{}^3D_1$
		(1.00)	0.50	1.50				
11	5100	(0)			1.10			$^3P_2{}^3D_3$
		(0)	(0.16)	(0.33)	1.00	1.17		
			1.33	1.50	1.67			
12	5020		(0.67)		1.29			$^3P_2{}^3D_2$
		(0.33)	**(0.67)**	0.83	**1.17**	**1.50**	1.83	
13	4969	(Not observed on plate)						$^3P_2{}^3D_1$
		(0)	(1.00)	**0.50**	1.50	2.50		
14	4924	(0)	1.97					$^3S_1{}^3P_0$
		(0)	2.00					
15	4858	(0.55)	1.47	2.02				$^3S_1{}^3P_1$
		(0.50)	1.50	2.00				
16	4618	1.83	(0)	1.92				$^3S_1{}^3P_0$
		2.00	(0)	2.00				
17	4585	(0)	(0.50)	**1.02**	1.52			
		(0)	(0.50)	**1.00**	1.50	2.00		$^3S_1{}^3P_2$
18	4330	(0.93)	0.99	2.00				$^3S_1{}^1P_1$
		(1.00)	1.00	2.00				

* NATIONAL RESEARCH FELLOW.

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THE STRUCTURE OF CERTAIN BANDS IN THE VISIBLE SPECTRUM OF BORON MONOXIDE

BY FRANCIS A. JENKINS*

JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY

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In 1913 Lord Rayleigh observed that when the vapor of boron trichloride is admitted into active nitrogen a bright greenish blue "flame" is obtained, the spectrum of which shows many clearly defined bands. The heads of these bands were then measured by Jevons[1] on quartz spectrograph plates of medium dispersion. More recently Mulliken[2] made a comprehensive study of this spectrum in connection with his verification of the isotope effect in electronic bands. Remeasurement of the heads, using quartz and glass spectrographs, permitted the complete identification of the fainter band systems due to the less abundant isotope of boron, and a partial measurement of structure lines in the bands of shorter wavelength. The magnitude of the isotope effect showed that the emitting molecule is the monoxide of boron, BO, which agreed with the observation that a small quantity of oxygen must be present in the active nitrogen to obtain the bands with any intensity. The spectrum consists of three electronic systems, the α bands extending from the extreme red to the near ultra-violet with quadruple heads shaded toward the red, the β bands in the further ultra-violet with single heads also shaded toward the red, and a much weaker "combination" system lying among the α bands with (apparently) double heads shaded toward the violet.

The active nitrogen source has now been arranged to give sufficient intensity for high-dispersion photographs, using exposures up to 10 hours, and it is the purpose of this communication to discuss the structure of the α bands as revealed on plates taken in the first and second orders of the 21-foot Rowland concave grating in this Laboratory. The dispersion is about 0.95 Å per mm. in the second order.

Plate 1 shows enlargements of three of the stronger α bands taken from first order plates. The designations (0, 1), (0, 0) and (1, 1) refer to the initial and final vibrational quantum numbers of each band. For the (0, 1) band a Fortrat diagram is given, with the total rotational quantum number, j, as ordinates. In each complete band there are evidently two origins, with four series proceeding from each. An unusual feature of this structure is the presence of two central branches of predominating intensity in each sub-band, other examples of it having been recently found in the CO^+ comet-tail bands[3] and NO third positive bands.[4]

In theoretically interpreting the occurrence and form of the observed branches we consider the rotational energy terms, between which transi-

tions occur according to the selection rule $\Delta j = 0$ or ± 1, giving rise to the actual frequencies referred to the band origin. The evaluation of these terms (except for an additive constant) may be carried through by certain combination relations, and when the latter are established it becomes a matter of the theoretical representation of the observed values of the terms. Since we are here primarily interested in the interpretation of the band

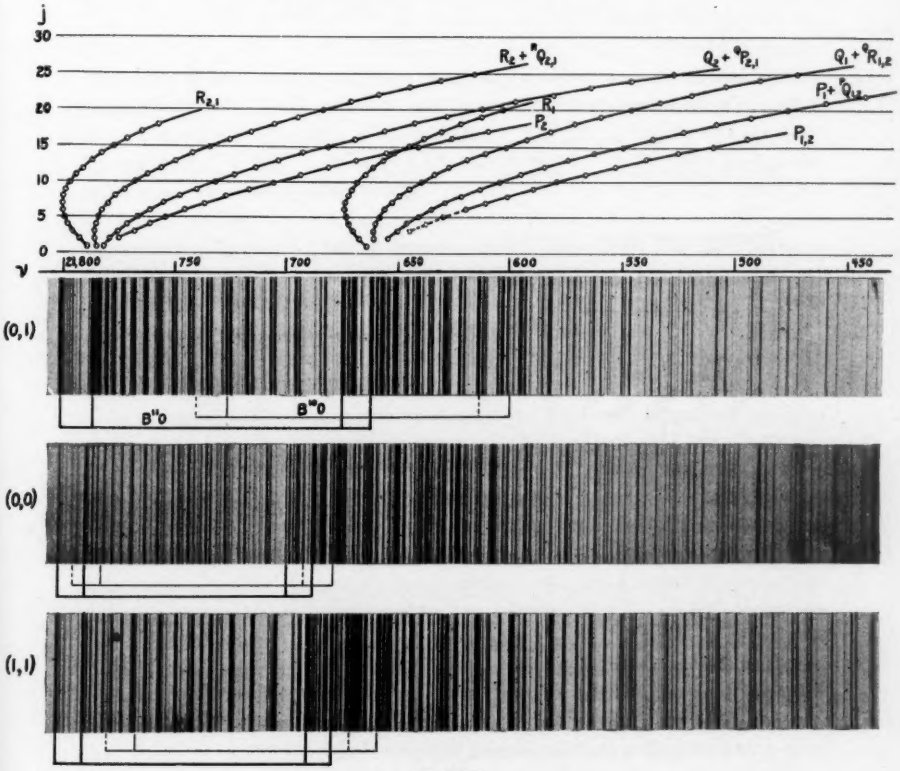

PLATE 1

Bands of the α system of boron monoxide.

structure, the wave-length and frequency data will be omitted, and only agreements in the combination differences which have a bearing on the term scheme will be considered. More complete data of an experimental nature will be published later.

The recent important work of Mulliken[5] and Hund[6] has resulted in a correlation of the structure of bands with the nature of the initial and final electronic states involved. The quantum numbers σ and ρ corre-

sponding to electronic angular momentum parallel and perpendicular, respectively, to the nuclear axis appear to have certain characteristic values for a given term-type. Thus for a $^2P \longrightarrow {}^2S$ transition, under which are classified the α bands of BO,[7] as well as the ZnH, CdH, HgH,[8] MgH, CaH ("A" bands),[9] CN (red system) and CO^+ (comet-tail) bands,[7,10] we expect the following formulæ to represent the rotational terms:

$$\begin{array}{cc} \text{Initial state } (^2P) & \text{Final state } (^2S) \\ F'(j) = B'(j^2 - \sigma'^2) + \ldots & F''(j) = B''(j - \rho'')^2 + \ldots \end{array} \quad (1)$$

Here σ' has the values $^1/_2$ for $^2P_1$ and $1^1/_2$ for $^2P_2$, while ρ'' is approximately $\pm{}^1/_2$. The existing material seemed to indicate that[8] in certain cases

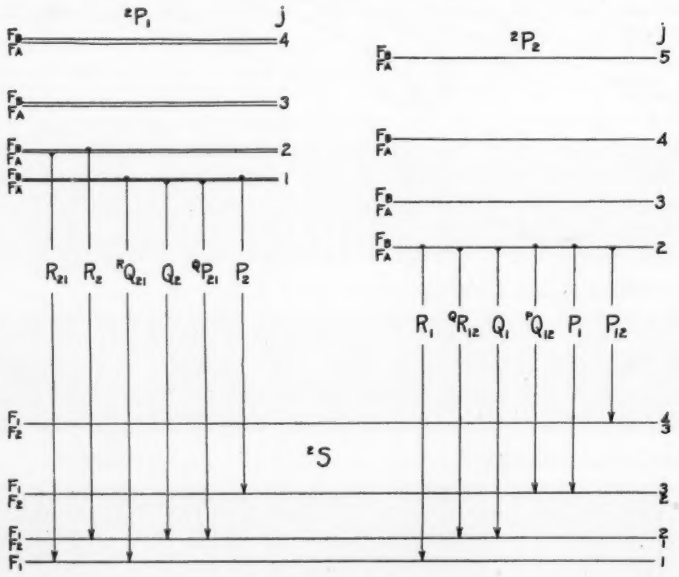

FIGURE 1
Term scheme showing first lines of each branch.

$\epsilon(= |\rho|)$ is exactly $^1/_2$ in the final state, which results in the complete coalescence of certain branches, giving only eight of the possible twelve in a complete band. In the bands of zinc, cadmium and mercury hydrides, however, all twelve are distinct. That the condition for coalescence is accurately met in the bands here considered is evidenced by the fact that lines of the two central branches of a sub-band remain strictly single throughout their course.

The arrangement of rotational terms for these bands which has been found to be required by the application of the combination principle is

represented schematically in figure 1. The first few rotational levels are drawn to scale for each of the three (arbitrarily spaced) electronic levels without vibration, and the transitions which are responsible for the first lines of each branch are shown by the vertical arrows. The notation used for the lines was kindly suggested to the writer by Prof. R. S. Mulliken, who has developed it in connection with a systematic study of bands of the $^2S-^2P$ and related types.

As represented in figure 1, the P_2 sub-level lies below P_1, that is, the doublet is inverted. This conclusion rests upon evidence from the number of missing lines near the origin in each of the two sub-bands. Aside from intensity relations, it is only in this respect that the values of σ are manifest when ϵ is not appreciable. The condition $j \geqq \sigma$ in the initial state requires that where $\sigma' = {}^1/_2(S-P_1$ sub-band) there shall be one missing line in the otherwise continuous series formed by the branches Q_{21} and Q_2, and two in that formed by R_{21} and P_2. On the other hand, where $\sigma' = 1^1/_2(S-P_2)$ there should be three missing lines in the Q_1-Q_{12} series, and also three in the R_1-P_{12} series. As far as can be determined by visual inspection of the plates, the required lines are absent if the higher frequency sub-band is denoted $S-P_1$. On account of the greater relative intensity of the Q branches, the evidence for the missing lines is much more conclusive for them than for the weaker R and P branches.

In support of this designation of the higher and lower frequency systems as $S-P_1$ and $S-P_2$, respectively, we have also the fact that the rotational levels of the P_1 state show a fine-scale doubling (not considered in Eqs. (1)), while the P_2 levels remain single with increasing j, as far as can be determined. This is the condition found in the case of the analogous ZnH, CdH and HgH bands, where, however, the ^2P doublet is normal. The rotational doubling in the P_1 levels shows itself as a small combination defect between the differences obtained between the Q_{21} and Q_2 branches and those between R_{21} and Q_{21} or between Q_2 and P_2. The order of magnitude of this doubling, which is exaggerated 10-fold in figure 1, may be seen from the first three columns of table 1, in which the values of column (2) are evidently slightly larger than those of the other two. In spite of this doubling, we still have the complete coalescence of branches which was mentioned above, owing to the "crossing over" rule.

This is shown in figure 1 by the fact that while in the main branches (single subscript) the R and P transitions are from F_B to F_2 levels, the Q transitions are from F_A to F_2. The relations are exactly reversed in the satellite branches (double subscript). This distinction between "main" and "satellite" branches results from analogy with other bands where the satellite lines are relatively much weaker, although in the present instance, which approaches case (a) of Hund[6] they are as intense as the lines of the main branches.

TABLE 1

COMBINATION DIFFERENCES FROM (0, 1) BAND

	(1) $R_{21}(j) - Q_{21}(j) < \Delta_1F_2'(j)$	(2) $Q_{21}(j+1) - Q_2(j) > \Delta_1F_2'(j)$	(3) $Q_2(j+1) - P_2(j+1) < \Delta_1F_2'(j)$	(4) $R_{11}(j-1) - Q_2(j) = \Delta_2F_1''(j)$	(5) $R_{21}(j) - Q_2(j-1) = \Delta_2F_2'(j)$	(6) $\frac{\Delta_2F_2'(j)}{j}$
2	7.03	7.06	7.05	....	....	....
3	9.83	9.94	9.80	17.55	16.99	5.66
4	12.68	12.84	12.58	24.51	22.64	5.66
5	15.43	15.72	15.40	31.61	28.30	5.66
6	18.33	18.53	18.28	38.58	33.93	5.65
7	21.00	21.42	21.01	45.71	39.70	5.67
8	23.89	24.23	23.81	52.52	45.24	5.65
9	26.66	27.07	26.68	59.66	50.88	5.65
10	29.43	29.93	29.40	66.61	56.61	5.66
11	32.21	32.79	32.21	73.56	62.19	5.65
12	35.01	35.62	....	80.57	67.83	5.65
					Av.	$5.66 = 4B_0'$

j	(7) $R_1(j) - Q_1(j) = \Delta_1F_1'(j)$	(8) $Q_1(j+1) - Q_{12}(j) = \Delta_1F_1'(j)$	(9) $Q_{12}(j+1) - P_{12}(j+1) = \Delta_1F_1'(j)$	(10) $R_1(j-1) - Q_{12}(j) = \Delta_2F_1''(j)$	(11) $R_1(j) - Q_{12}(j-1) = \Delta_2F_1'(j)$	(12) $Q_{21}(j+1) - Q_2(j)$ [(0, 0) band]
3	9.60	9.68	....	17.53	16.62	10.03
4	12.44	12.45	....	24.53	22.12	12.88
5	15.30	15.12	15.29	31.52	27.75	15.60
6	17.98	17.97	17.98	38.65	33.10	18.54
7	20.67	20.77	20.77	45.52	38.65	21.33
8	23.45	23.55	23.57	52.52	44.22	24.20
9	26.22	26.27	26.31	59.53	49.76	27.07
10	29.02	29.03	28.96	66.57	55.29	29.89
11	31.78	31.84	31.75	73.63	60.81	32.75
12	34.54	34.61	34.66	80.62	66.38	35.61

For the evaluation of the intervals between the rotational terms, we have in this case four different types of combinations, which should all give agreement when an identical set of terms is concerned. First, there are the combinations between the lines of the several branches of a given sub-band. These are illustrated in table 1 by the agreement between columns (1) and (3) and between columns (7), (8) and (9). Second, the identity of the final state of the two sub-bands may be shown by combinations between the lines of each, as evidenced by the correspondence of columns (4) and (10). The required differences in both of these types may be read directly from the term scheme of figure 1. The third type correlates complete bands which have a vibrational state (initial or final) in common. Thus the initial levels of the (0, 0) and (0, 1) bands are identical, and hence the corresponding combination differences must agree, as shown in columns (2) and (12). A fourth type of agreement would result from the fact that the α and β systems have a common final electronic state, and that the initial state of the combination system is identical with the initial state of the β system, while its final state is the same as the

initial state of the α bands. The resulting relations would constitute very exacting test of the combination principle, but cannot be considered here, since no measurements have as yet been made on the β and combination systems.

Examination of the quantities given in table 1 will show that they are in every respect in agreement with the requirements of the term-formulas of equations 1. Thus we find[11]

$$\begin{aligned} \Delta_1F'(j) &= 2B'(j + {}^1/_2) + \ldots; & \Delta_2F'(j) &= 4B'j + \ldots \\ \Delta_1F''(j) &= 2B''(m + {}^1/_2) + \ldots; & \Delta_2F''(j) &= 4B''m + \ldots \end{aligned} \qquad (2)$$

where $m = j - {}^1/_2$ for F_1 states and $j + {}^1/_2$ for F_2 states. A simple and rather accurate method of evaluating the constants B' and B'', therefore, consists in assuming that the ΔF values obey the linear relations of equation (2), as illustrated in column (6) of table 1.

In this way the constants were determined from data on both components of the (0, 1) and (0, 0) bands, and also the higher frequency component of the (0, 0) band of the fainter isotopic system of $B^{10}O$. Neglecting the rotational doubling, we may then represent the four branches, for example, of the $S-P_1$ sub-band, by the simple formulas.

$$\begin{aligned} R_{21}(j-1) &= \bar{\nu}^0 - 2B'' + 3B''j + Cj^2 \\ R_2(j-1) &= Q_{21}(j) = \bar{\nu}^0 + B''j + Cj^2 \\ Q_2(j) &= P_{21}(j+1) = \bar{\nu}^0 - B''j + Cj^2 \\ P_2(j+1) &= \bar{\nu}_0 - 2B'' - 3B''j + Cj^2, \end{aligned}$$

where $\bar{\nu}^0 = \nu^0 - B'\sigma^2 - B''\epsilon^2$ and $C = B' - B''$.

The quantity B_0, which is the value of B for the state $n = 0$, is given in table 2 for the initial and final states. It determines the value of I_0, the moment of inertia for the vibrationless molecule, since $B_0 = h/8\pi^2I_0$. The calculated values of I_0, together with the corresponding values of the internuclear distance, r_0, are also entered in table 2. Recent work[12] has shown that the difference in B_0 for $^2P_1$ and $^2P_2$ states does not indicate a real difference in the moment of inertia, but is due to another cause. Thus a single value of I_0, and of r_0, which is very closely the mean of the two apparent values of table 2, suffices for the sub-states of the doublet. As expected, the moment of inertia of $B^{10}O$ is considerably smaller than that

TABLE 2

CONSTANTS OF BO MOLECULE FROM DATA ON BAND STRUCTURE

	$B^{11}O$			$B^{10}O$		
	$^2P_1$	$^2P_2$	^2S	$^2P_1$	$^2P_2$	^2S
B_0	1.412	1.383	1.767	1.495	.....	1.870
I_0	19.62×10^{-40} gr. cm.^{2}	20.02	15.68	18.52	.....	14.82
r_0	1.351×10^{-8} cm.	1.364	1.207	1.352	.....	1.208

of $B^{11}O$, but the nuclear separation, computed using the reduced mass, is identical for the two isotopic molecules. This results, of course, from the fact that isotopic atoms behave alike in all matters which depend on the configuration of the external electrons. The agreement for both initial and final states constitutes a satisfactory confirmation of the first-order rotational isotope effect.

The study of isotopic band systems, which differ only by virtue of the difference in the nuclear masses of the emitting molecules, promises to shed new light on various aspects of band spectrum theory and, in fact, the molecule of BO is at present the most favorable case known for such an investigation. Many of the theoretical inferences to be drawn will require a much more extensive measurement of the two isotopic band systems than has yet been made. However, the question of the absolute values of the effective vibrational quantum numbers may be tested very simply by a consideration of the positions of the origins of the (0, 0) bands of the isotopic systems. Thus if the effective quantum numbers are assumed to be integral, beginning with zero, the two origins should coincide. From a comparison of the equations obtained from measurements on the band heads, however, Mulliken[2] concluded that this is not the case and that the vibrational energy should probably be represented as a function of $(n + {}^1/_2)$,where $n = 0, 1, 2, \ldots$ This is in agreement with the requirements of the new quantum mechanics. The present work confirms this view very definitely, since the two (0, 0) bands were found to be distinctly displaced, that for $B^{10}O$ lying further to the red, as shown on plate 1. The origins of the higher frequency sub-bands of both were computed, the results being 23,647.11 for the stronger ($B^{11}O$) system, and 23,638.46 for the weaker ($B^{10}O$). The difference, 8.65 $cm.^{-1}$, is to be compared with the value 9.12, calculated with the assumption that the states $n = 0$ retain a vibrational energy of ${}^1/_2h\omega_0(1 - {}^1/_2x)$, and using the constants ω_0 and x determined by Mulliken.[2] The agreement is very good considering the various quantities involved, although it may be that the small discrepancy indicates an electronic isotope effect.

In conclusion it may be well to recall the remarkable similarity of the BO bands to those of CO^+, which is probably to be attributed[7] to the identical number of external electrons in the two molecules, and which is still further emphasized by the present study of the structure of the α bands of BO. This resembles the structure of the CO^+ comet-tail bands in every detail, as will be seen by reference to the reproduction given by Baldet.[3] Furthermore, the separation of the heads of the sub-bands, 126 $cm.^{-1}$, is equal for the two systems. CO^+ gives two other band systems, the negative Deslandres group of carbon,[13] and the Baldet-Johnson combination bands, which show a complete analogy with regard to position and structure with the β and combination systems, respectively, of BO.

The writer wishes to express his indebtedness to Prof. R. S. Mulliken, at whose suggestion the photography of the bands was undertaken, and who has on many occasions given valuable advice on various questions.

* NATIONAL RESEARCH FELLOW.

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*PRESSURE PHENOMENA OF THE MUCRONATE ANODE**

BY CARL BARUS

BROWN UNIVERSITY, PROVIDENCE, R. I.

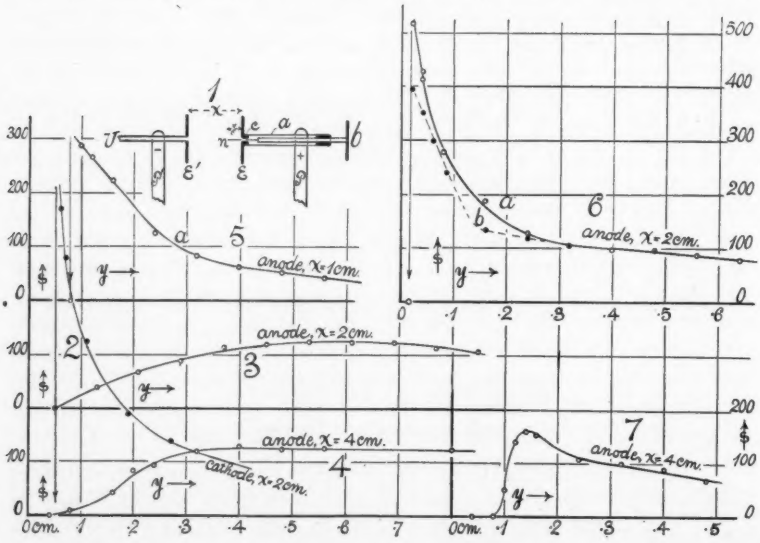
Communicated June 11, 1927

1. *Introductory.*—The date of the preceding paper showed the pressures produced by a convection current emanating from the cathode, when its center is provided with a slightly projecting needle point. In the present experiments the mucronate electrode E (see Fig. 1, E,E' electrodes, n needle pt., b micrometer screw, interferometer U-gauge beyond U) is an anode. Let x be the width of the spark gap, y the projection of the needle, and s (roughly in 10^{-6} atm.) the pressure of the wind from n impinging on the perforated cathode E'. A small Winshurst, capable of delivery, $^1/_2$ inch sparks energizes the posts P and P' and appurtenances.

2. *Data.*—The former results with the cathode point are recorded in figure 2 (for $x = 2$ cm.), for comparison. The cusp of the graph is often over $s = 600$ high. It differs, therefore, strikingly from the first of corresponding anode graphs, *caet. par.*, figures 3 and 4, obtained consistently throughout many repetitions. There is no suggestion of a cusp for small y values, but the graphs rise leisurely to flat maxima. From these one would infer that an anode potential maximum is absent.

However, in figure 5 for a spark gap $x = 1$ cm. the characteristic form reappears, though the graph seems to be made up of two roughly linear parts abruptly joined at A. One notes that if $y = x$, $s = 0$ nearly, which is also roughly the case in figures 3 and 6.

The results of figure 5 led me to suspect that there might be something amiss in the apparatus which was, therefore, generally overhauled with the results shown in figure 6 curve A, though at times the form b was obtained from very slight interference with the apparatus. What the nature of the difference of figures 3 and 6 may be, I have been unable to detect; but since anything like sputtering or purring in the discharge



is fatal to high s values, and since this condition sets in casually, such occurrences are probably in question. The cusp in figure 6 is but slightly lower than in figure 2 for the cathode, though the former is much nearer the electrode.

Figures 4 and 7 for $x = 4$ cm. show a similar change in the form of graph obtained. Again in figure 7 the cusp is rounded in the way also observed in the cathode curves. The crest, however, is now further away from the electrode, all of which illustrates the capriciousness of these sparking phenomena.

If we join figures 2 and 6, reversing either one or the other, we get a diagram recalling to some extent the distribution of potential gradient or field strength in a vacuum tube, though in the present instance we are dealing merely with the convection currents between mucronate electrodes.

The great difficulty with the work is the fluctuating behavior of the machine, so that long observation is necessary to obtain the mean fringe deflection at each point.

Thus it appears that sharp surfaces of max. and of min. potential, respectively, surround the anode and cathode, the surfaces confronting each other and about half a mm. from the electrode plates. If the needle point of the mucronate electrodes penetrates these limiting surfaces a convection current is observed whose strength decreases rapidly as the needle protrudes further. At the surface there is usually a cuspidal maximum of current. If the needle point lies within the surface, it is inert and spark discharge, sputtering or purring may occur between any points of the electrode, while the convection current is absent. In how far these results conform with the usual equations for space charges I have yet to learn.

* Advance note from a Report to the Carnegie Institution of Washington, D. C. See these PROCEEDINGS.

ON THE LAG OF THE KERR EFFECT

BY J. W. BEAMS* AND ERNEST O. LAWRENCE*

YALE UNIVERSITY

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Introduction.—Kerr discovered that certain liquids placed in an electrostatic field exhibit slight double refraction. The generally accepted explanation[1] of this phenomenon, called the Kerr effect, is that molecules possess definite optical anisotropy and that an electric field exerts an orientative influence on the molecules of the liquid, thereby giving rise to general optical anisotropy of the medium. Langevin originally assumed that the molecules are both optically and electrostatically anisotropic, the orientative action of the field arising from the couple exerted by the field on the electric moment induced along a preferential direction of the molecule. Born later took into account also the orientative couple of the electrical field due to the permanent moments of the molecules. A rather wide range of experimental facts indicate that this view of the mechanism of the Kerr effect is essentially correct. For example, Raman and Krishnan[2] have recently shown that data on the scattering of light by liquids, which are measures of the optical anisotropy of the molecules, fit in very well with estimates of molecular optical anisotropy made on the basis of the orientation theory and Kerr effect data.

Accepting the view that the orientation of the molecules by the electric

field is responsible for the Kerr effect, one immediately infers that the Kerr effect is not instantaneous. That is, the molecules do not assume random positions at the same instant the electric field is relaxed because of opposing viscous and inertial forces. The orientation hypothesis leads to the conclusion that the time taken for the molecules to assume random positions, the so-called "relaxation time,"[3] varies directly as the frictional force (viscosity) exerted by the molecules on each other and inversely as the temperature of the medium. Thermal agitation is responsible for the dispersing of the array—and it is more violent at higher temperatures. Assuming the frictional force on a single molecule of water to be the same as that on a sphere of from $1/10^8$ cm. to $2/10^8$ cm. radius moving in a continuous medium having a coefficient of viscosity the same as observed macroscopically for water, it is calculated that the relaxation time is of the order of magnitude of from 10^{-10} sec. to 10^{-11} sec. It has been shown recently,[4] however, that for some liquids the observed lag of the Kerr effect (which, at first sight at least, one would expect to be of the same order of magnitude as the defined "relaxation time") is considerably greater—as much as $6(10^{-9})$ sec. for ethyl ether. The observations also indicated that the double refraction of the medium does not decay exponentially with the time after cut off the electrostatic field as the theory indicates, but that the double refraction persists for a definite length of time after cut off and then in a much shorter time interval disappears.

It is evident that experimental facts concerning characteristics of the lag in the Kerr effect would be of great value as a guide to a formulation of a satisfactory theory of the influence of electric fields on molecules in gases or liquids—leading thereby to an enhanced conception of the nature of inter-molecular forces. With this in mind we have carried through the following experiments.

The Experiments

These experiments involved measuring the differences in the lag of the Kerr effect behind the electric field for the liquids in two Kerr cells K_1 and K_2. The procedure of this measurement has been described elsewhere.[4] However, to recall it to mind, it may be remarked briefly that (referring to the diagram) the two cells K_1 and K_2 are so oriented between crossed Nicol prisms N_1 and N_2 that they produce equal and opposite ellipticity of the plane polarized light from N_1 when the electric field between the plates of the two cells are equal. Under these circumstances no light passes N_2 when the same electrostatic voltage exists across both cells simultaneously. A transformer T charges a condenser C which is discharged across the spark gap SG, the light therefrom passing through the Nicol N_1 and through the Kerr cells K_1 and K_2 and (if ellipticity of the plane

polarized light is produced on passing through K_1 and K_2) through the crossed Nicol N_2 to the observer's eye or through a spectroscope S to the eye. The plates of the cells K_1 and K_2 are connected across the spark gap by leads of variable length, T_1 and T_2, so that during charging of the condenser a voltage across the plates is also impressed. On discharge of the spark, the voltage across the plates is suddenly relaxed at a time after the beginning of the spark equal to the wire paths connecting plates to the spark gap divided by the velocity of light. Because of the compensating effect of both Kerr cells no light would emerge from N_2 in case (1)

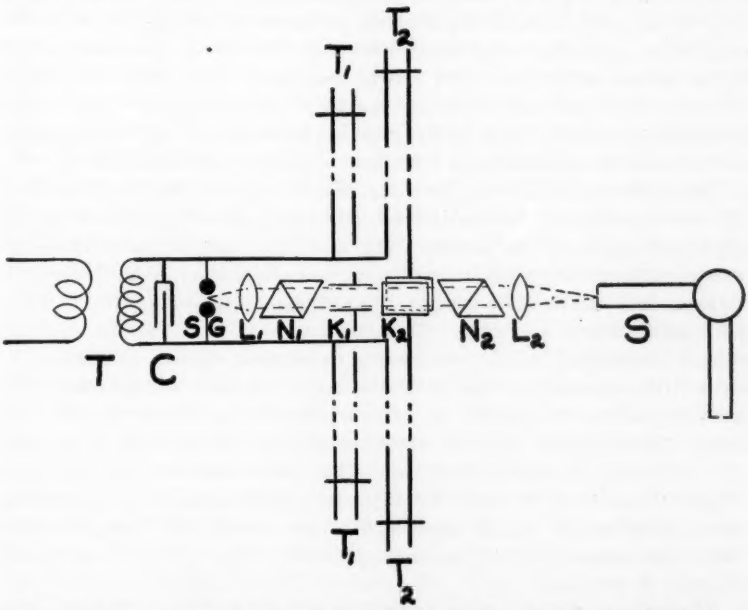

Diagram of the experimental arrangement for measuring the lag in the Kerr effect.

the lags of the disappearance of the Kerr effects in the two cells behind the cut off of the electric field between the plates were equal and (2) the wire paths to the two cells from the spark gap were equal. In case, however, the wire paths to the two cells were the same but the lags were different there would exist a time interval during which the liquid in one of the cells only is doubly refracting. Such a situation would evidence itself by light emerging from N_2. By increasing the wire path to the cell containing the liquid having the sorter lag the effect of difference of lags could be compensated. It is clear that the difference in the time lags is equal to the differences of the wire paths to the two cells from the spark gap divided

by the velocity of light—when the wire paths are so adjusted that no light emerges from N_2. The measurement of the lag differences, therefore, consisted in observing the wire paths differences necessarily introduced to extinguish the light as observed through N_2.

The Lag of the Kerr Effect as a Function of the Wave-Length of the Light.—The light emerging from N_2 was resolved by the spectroscope S and measurements were made on the differences between the lags of carbon bisulphide and several liquids for various wave-lengths of visible light. *It was found that for all wave-lengths the lags were the same and were as follows:*

Bromoform $3.3(10^{-9})$ sec. Chloroform $3.8(10^{-9})$ sec. Ethyl ether $6(10^{-9})$ sec., the values being the lags in excess of the lag in carbon bisulphide. A previous experiment[5] indicated that the absolute value of the lag in carbon bisulphide is very small—less than $3(10^{-9})$ sec. The values for chloroform and bromoform are probably correct to $5(10^{-10})$ sec. while the value for ethyl ether is hardly more accurate than to 10^{-9} sec. because of its low Kerr constant and attendant experimental difficulties.

The Influence of Electric Polarity of the Molecules on the Lag of the Kerr Effect.—It is known[6] that bromoform, chloroform and ethyl ether are polar while carbon bisulphide is not. The first three substances exhibit lags considerably greater than a possible lag in carbon bisulphide, the magnitude of their excess being roughly proportional to the magnitude of their permanent electric moments. This fact suggested that the lag may be directly dependent on the existence of permanent dipoles in the molecules. To substantiate this view the lag in benzene was measured relative to carbon bisulphide—as benzene likewise is known to be non-polar. It was found that this substance exhibits no appreciable lag relative to the lag of carbon bisulphide. The measurements were especially difficult because of the small Kerr constant of benzene but it is probable that a difference in lags as great as 10^{-9} sec. would have been detected. This result makes it highly probable that *only polar molecules exhibit lags as great as 10^{-9} sec.*

The Influence of Temperature on the Lag of the Kerr Effect.—The theory of "relaxation times," which presumably are proportional to the "lags" here measured, leads to the conclusion that the lags are proportional to the viscosity and inversely proportional to the temperature. To test this, chloroform was placed in both Kerr cells and by a suitable cooling system the liquid in one of the cells was cooled from room temperature, 25°C. to −5°C. It was found that when the two cells were at the same temperature and the wire paths were equal no light emerged from N_2 and that when one of the cells was cooled light did pass the combination. By shortening the wire path to the cooled cell, again the light through N_2 was extinguished, indicating a greater lag in the cooled cell. Careful measurements showed the difference in the lags between room temperature

and -5°C. to be about 2 (10^{-9}) sec. Here again the measurements were difficult and the magnitude of the value cannot be trusted to within 10^{-9} sec. The important thing, however, is that a *definite increase in the lag with temperature was observed.* It was also noticed that the lag seemed to increase more rapidly than the reciprocal of the temperature indicating therefore, on the basis of the theory, that frictional forces on the molecules increased with decrease of the temperature of the liquid.

Discussion

On the orientation hypothesis it is concluded that the lag in the Kerr effect is due wholly to molecular, frictional and inertial forces which give rise to finite times of orientation and, therefore, that the lag is quite independent of the wave-length of the light. Our observations insofar as they verify this conclusion support such a theory of the Kerr effect. The fact that only polar molecules exhibit appreciable lags is not so apparent from the theory because, presumably, non-polar molecules assume definite arrays when producing a Kerr effect in a liquid, and it seems reasonable to expect that the time required for assuming random orientations would be of the same magnitude for such a non-polar array as for a group of oriented polar molecules. However, an explanation of the experimental observations is probably to be sought in the influence of the polarization of the liquid as a whole in tending to maintain the spacial array of the molecules. It is probable that the polarization due to the induced moments disappears more rapidly than the polarization arising from permanent doublets in the molecules and, therefore, that the forces tending to resist thermal disruptions of the array persist longer in polar liquids. The fact that the lag increases with decrease in temperature is emphatic in support of the hypothesis of molecular array. The theory in its present form hardly can account for the manner in which the Kerr effect decreases after cessation of the electric field. Our observations indicate that the Kerr effect persists quite undiminished for a definite time after relaxation of the field and then in a much shorter time disappears—as though a condition of instability of the molecular array is attained at a definite time after the relaxation of the electric field at which moment the array suddenly collapses. It is not at all inconceivable that this collapse of the orientation of the molecules proceeds in a manner described by the theory—decreasing to $1/e$th of its value in from 10^{-10} sec. to 10^{-11} sec.

We wish to thank Professor P. Debye for emphasizing to us the importance of determining the dependence of the lag of the Kerr effect on temperature. We also wish to thank Mr. T. H. Rider of the department of chemistry for purifying a quantity of benzene and bromoform for our experiments. Finally, we record with pleasure our indebtedness to Professor W. F. G. Swann for his interest in this work.

* NATIONAL RESEARCH FELLOW.

[1] A good account of the subject by P. Debye is contained in Marx's *Handbuch der Radiologie*, Bd. 6, pp. 754–776.

[2] C. V. Raman and K. S. Krishnan, *Phil. Mag.*, **3**, pp. 713–735.

[3] The relaxation time is defined as the time required for the orientation of the molecules to diminish to 1/*e*th of the extent of the orientation when the field is on.

[4] Beams, *J. O. S. A. & R. S. I.*, **13**, p. 597; Beams and Allison, *Phil. Mag.* (in press).

[5] An experimental investigation of the lag in the photo-electric effect led to the conclusion that the sum of the lag of the Kerr effect in carbon bisulphide and the lag of the photo-electric effect from a potassium surface is not greater than $3(10^{-9})$ sec. We read a paper on this research at the April meeting of the American Physical Society (abstract in press) and shall publish details later.

[6] O. Blüh, *Phys. Zeit.*, No. 8, p. 226 (1926); C. P. Smyth, *J. Am. Chem. Soc.*, **46**, p. 257 (1924); R. Sänger, *Phys. Zeit.*, No. 17, p. 556 (1926).

MOBILITIES OF IONS IN ACETYLENE HYDROGEN MIXTURES

BY L. B. LOEB AND L. DU SAULT

PHYSICAL LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY

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Introduction.—In a recent paper by Erickson[1] on the variation of mobilities of gas ions with age in acetylene results of theoretical importance were obtained. The important result from the viewpoint of this work was the discovery that apparently *neither the positive nor the negative ion in acetylene showed a change in mobility with age within time intervals greater than 0.002 second, while at the same time* the mobility was *slightly greater for the negative ion than for the positive ion.* In H_2, Erickson[2] had earlier found an aging effect on the positive ion in which the mobility changed in time from a value a *little less than that of the negative* to the value normally ascribed to the positive ion, which is about 0.60 that of the negative ion. In all other gases, the positive and negative ions had the *same initial mobility within the limits of experimental error*, and the positive ions with age acquired that mobility less than that of the negative ion, which is generally observed. Gases in which the final negative ion has a mobility less than the positive ion have not been investigated although experiments on this subject are being undertaken in this laboratory.

The conclusion which Erickson draws from the aging experiments is that the initial ions, positive and negative, are monomolecular ions whose mass influences the mobility to a negligible amount, but whose mobility depends on the diameter or "apparent" diameter of the ion. The aged ion has been shown by Erickson to be generated in a unitary process, no intermediate steps being observed. This led him to the conclusion that

the aged positive ions were bi-molecular ions. Inasmuch as Erickson does not assume differences of the attractive forces due to the strongly divergent[3] electrical fields of positive and negative ions on molecules of the gas which alter the mobility, the fact that the initial mobility of the positive ion in H_2 is less than that of the negative ion, and that the apparently unaged ions in acetylene have different mobilities, leads to difficulties. The assumptions used by Erickson force one to assume, in these cases, that the initial positive ion in H_2 is, when measured, already polymolecular and grows still larger, and that the acetylene ions are already aged, or age in a very short time as compared to those for other gases.

The recent work of one of the writers[4] has shown that in studying mobilities of mixtures of H_2 and other gases, specific clustering effects make themselves known by very marked changes in mobility in the mixtures for traces of the active gas added. NH_3, which can form an NH_4^+ ion in solution, acts to increase the mobility of the positive ion in H_2, indicating, on Erickson's view, that the NH_4^+ ion, if it forms, has a smaller diameter than the molecule usually attached to the positive hydrogen ion making the normal ion. In view of the close values of the positive and negative mobilities found by Erickson in C_2H_2, and the fact that C_2H_2 forms complex acetylide ions with some metals in solution, it was thought of interest to study C_2H_2 by the method of C_2H_2-H_2 mixtures. Such a method would at once indicate any intense attractions of ions for acetylene as would have to be assumed to account for the quick aging if it existed, and it would also indicate the formation of special small ions as with NH_3.

Experimental Procedure.—The measurements were made exactly as those detailed in previous papers,[4] except for minor improvements in technique. The same measuring instruments as used in earlier work were used throughout.

The acetylene was generated from commercial carbide, Miner's Lamp brand of the National Carbide Company, by dropping distilled water onto the carbide that was in a previously exhausted flask. It was collected in a 5 gallon glass carboy whence it passed into a purifying train. This consisted of two tubes each a meter long. The first one contained chloride of lime followed by powdered calcium oxide and calcium chloride. The second contained anhydrous calcium chloride and phosphorous pentoxide. The gas then passed through two traps cooled to $-70°$C. by frozen alcohol. From these it was condensed, by means of liquid air, in a pyrex glass trap connected to a manometer which could be isolated and evacuated. In the condensation of C_2H_2 which sublimes, much trouble was encountered due to the fact that the first acetylene condensing forms a snowy non-conducting frost on the sides of the tube which slows the process of condensation. An iron magnetic scraper was sealed inside the tube so that the deposit could be scraped off as it formed. Even with this, the amount

of gas condensed seemed very capricious, and it was hard to decide just what amount had condensed out in the two hours allowed before fractionating it. After condensing the gas, the generator was cut off and the trap pumped to very low pressures at liquid air temperatures. There was an appreciable vapor pressure at the temperatures used so that the more volatile impurities could not be as completely removed as desired. It was suspected that at times other more volatile hydrocarbons than acetylene were present. These were removed as much as possible and only the central portion of the distillate was used. Filling and mixing proceeded as before described, except that for some of the small percentages the gas was mixed with H_2 once, then the pressure was read and most of the mixture was pumped out to a desired pressure. The pressure was read again and then more H_2 added. The C_2H_2 forming from the carbide had the usual unpleasant odor. The purified C_2H_2, however, had a distinctly sweet odor which was not unpleasant but could not be identified with any organic substances within the writers' considerable experience. The nature of some of the mobilities observed indicated definitely that the acetylene was quite free from *electro negative* impurities like Cl_2, HCl, etc., and the suspicion is that the gas was fairly pure. Since the recent experiments of one of the writers, the word "purity" for such experiments has taken on a different meaning. The traces of impurity affecting results are such that they are not easily to be detected by chemical means so that one must speak with caution about the purity of gases in this field.

Mobilities of Ions in C_2H_2.—Heretofore, only one absolute measurement of the mobility of ions in this gas has been made. It was made on negative ions by Wahlin,[5] using the Rutherford method and photo-electrically generated ions. Erickson[1] does not give the absolute values for the mobilities for he was interested in the relative values only. The values obtained in this work are thus of interest. The mobilities were determined with an auxiliary field of 7.5 volts/cm., and with ions crossing at 34 volts/cm. for the positive and negative ions. Where results were obtained at other field strengths for + and − ions, they were corrected for the effect of the interpenetration of the fields,[6] on the basis of previous experiments on air, to the ratio of the field strengths above. The values obtained are as follows:

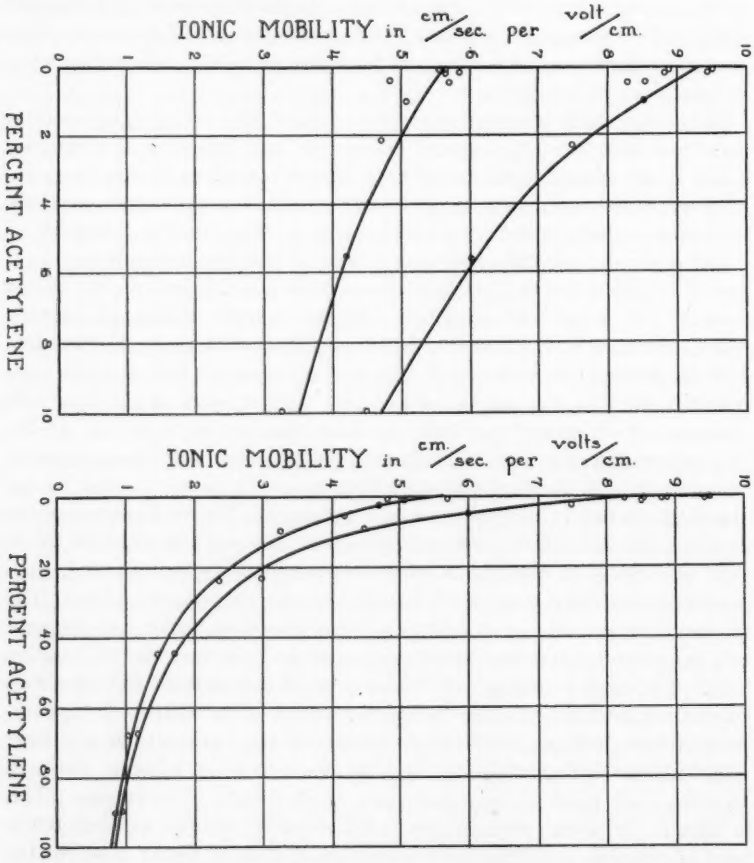
+ IONS	− IONS
0.800	0.850
0.738	0.857
0.785	0.830
0.795	0.830
0.795	0.852
0.795	0.844
0.800	
Av. 0.787 cm./sec. per volt/cm.	Av. 0.844 cm./sec. per volt/cm.

This corresponds to values of 0.708 cm./sec. per volt/cm. for positive and 0.769 cm./sec. per volt/cm. for negative ions on the accepted scale, where the mobility of the negative ion in air is taken as 1.8 cm./sec. per volt/cm. On the basis of the true absolute values of Loeb[6] and Tyndall and Grindley,[7] the values are 0.846 cm./sec. per volt/cm. for the positive and 0.906 cm./sec. per volt/cm. for the negative ions. The value found by Wahlin for the negative ion is 1.15 cm./sec. per volt/cm. on the absolute basis, and 0.96 cm./sec. per volt/cm. on the commonly accepted basis. This discrepancy seems serious. It is, however, easily explained in view of results to be discussed.

In the first three measurements, the negative ions in C_2H_2 gave normal mobilities at 630 mm. pressure. Owing to the difficulty of obtaining enough C_2H_2, in the fourth measurement, this was made at 50 mm. pressure. In place of the negative ions previously observed, *free electrons* were observed, even though the time for a carrier to cross was of the order of $^1/_{30}$ of a second. Wahlin had observed free electrons definitely below 40 cm. in his acetylene. These electronic carriers were present in the gas even after 24 hours in the chamber. The next sample of C_2H_2, in the fifth filling, gave 750 mm. pressure. It had not been as carefully fractionated. Here no electrons were observed. At 50 mm. pressure, free electrons were not obtained but the curves for negative carriers were of the dual sort observed by Wellisch[8] and later by Loeb,[9] indicating that 50% of the carriers were free electrons. In the last sample, a curve at 56 cm. pressure was obtained of the dual sort, the obvious free electronic portion of the curve amounting to 15% of the carriers present. The first portion of the curve, if one ignored the obviously electronic portion and took the intercept as is done for most measurements with small asymptotic feet, gave a mobility of 0.961 cm./sec. per volt/cm. for the negative ions. The mobilities estimated from the break point in the curve, which was of course not sharp, gave a mobility of 0.844 cm./sec. per volt/cm. for the negative ions. The high mobilities of Wahlin, in whose method free electrons played a greater rôle than in the gauze method of the writers, the appearance of free electrons at 500 mm. pressure in large proportions and their effect on the mobility curves, and the values of the mobility deduced therefrom all point to an explanation of Erickson's observations. This is that in Erickson's measurements his negative carriers were electronic part of the time and thus gave mobilities that were higher than for the positive ions. In fact, it seems fairly safe to assert that the negative and positive ions in acetylene, *once they have formed, have the same mobility.* The value of the mobility for ions in acetylene could then be set for both ions as 0.708 cm./sec. per volt/cm. on the accepted scale and as 0.846 cm./sec. per volt/cm. on the absolute standard of Loeb and Tyndall.

As regards the effects in H_2, the same may be said. It is probable that

the true mobility of the negative ion in H_2 is the same as that of the initial positive ion, and that the apparently high value observed by Erickson is due to the fact that in relatively pure H_2, electrons do not attach. This explanation was suggested by one of the writers in a previous paper. The greatest difficulty seems, therefore, to have been removed in the interpretation of Erickson's results in C_2H_2 and H_2.



Mobilities in C_2H_2-H_2 Mixtures.—The mobilities in mixtures of from 0.1% C_2H_2 to 100% C_2H_2 and H_2 were determined for positive and negative ions. The results are shown in the curves of figures 1 and 2. Figure 1 shows the values for percentages from 0 to 10% C_2H_2 and figure 2, for percentages from 0 to 100%. The smooth curves are the theoretical[10,4] curves computed, assuming the ordinary law of mixtures to hold, to wit—

$$K_c = \frac{100K_{H_2}K_{C_2H_2}}{(100 - c)K_{C_2H_2} + cK_{H_2}}$$

where c is the concentration of C_2H_2 in per cent, and K_{H_2} and $K_{C_2H_2}$ are the mobilities of the ions in the pure gases. The values of K_{H_2} and $K_{C_2H_2}$ chosen for these computations are, for C_2H_2, $K_{C_2H_2} = 0.787$ for positive ions and $K_{C_2H_2} = 0.843$ for negative ions, and for H_2, $K_{H_2} = 5.64$ for positive ions and $K_{H_2} = 9.33$ for negative ions. It is to be noted that K_{H_2} is 5.64 for positive ions. This is somewhat less than the values found for pure H_2 in the NH_3 experiments.[3] The cause of this is not certain. It probably lies in the purity of the H_2 used which was merely passed over a drying train of NaOH, $CaCl_2$, P_2O_5, and through the liquid air traps, this particular H_2 coming from a bomb that was only half full. The question of the purity of the H_2 and its effect on mobilities needs further elucidation and study. Suffice it to say that 10 cm. of this H_2 added to 50 cm. of pure C_2H_2 removed the free electrons found there. It is also possible that the effect of traces of impurities in the acetylene used so contaminated the chamber as to give the lower positive values in H_2. It may be stated that repeated pumping and filling did not materially change the value for these ions in H_2, indicating that it was probably not due to the C_2H_2 itself. For small concentrations of C_2H_2, the values of the mobilities were not very consistent. This may in part have been due to impurities, but it was probably largely due to the difficulty of measuring the small percentages accurately. If one overlooks the inconsistencies at low concentrations which seem to go in both directions, the mobilities observed in the mixtures follow the law of mixtures fairly well. It can be safely stated that, *within the limits of experimental error, the mobilities in the acetylene-H_2 mixtures follow the law of mixtures*. Deviations of the type observed in ether-H_2 mixtures occur for neither ion, and the effect looked for in which C_2H_2 markedly increases the mobility of the positive ion in H_2 is definitely absent. Thus no evidences of clustering in a marked form occurs for ions in C_2H_2-H_2 mixtures.

Conclusions.—These measurements indicate that the mobility of positive and negative ions in C_2H_2 is probably the same. Mobilities observed that are contrary to this, where the negative ion has the higher mobility, may be explained on the existence of free electrons as carriers in the early part of the careers of the ions. These results remove some of the difficulties in interpreting Erickson's results on C_2H_2 in terms of his theory of the mono and bimolecular ions. They also indicate a way out of his difficulty in the case of the difference between the mobilities of the negative ions and initial positive ions in H_2.

The measurements in mixtures give no certain indication of clustering or selective clustering of a marked nature on either ion in C_2H_2. The

mobilities follow the law of mixtures holding for non-reactive gases, as well as experimental uncertainties will permit. They give no ground for the suspicion that a very rapid aging takes place for ions in C_2H_2. Whether the theory of Erickson is correct or not is not indicated by these results. They merely remove some of the difficulties encountered in C_2H_2. A study of many other gases is needed, especially those where the negative ion has a lower mobility than the positive ion. The theory is liable to criticism from a theoretical point of view for it does not allow any latitude for the influence of the action of the electrical field of the ion on molecules on the mobility. The action of the field of the ion is assumed merely to cause the clustering. Whether or not the former effect, which must be present, can be included in the theory without seriously changing it, remains to be seen. It has not been needed thus far in accounting for the observed experimental facts which it has had to explain and has perhaps, therefore, been omitted.

[1] Erickson, H. A., *Physic. Rev.*, **28**, 372, 1926.

[2] Loeb, L. B., *J. Franklin Inst.*, **201**, 282, 1926; also Erickson, H. A., *Physic. Rev.*, **26**, 465, 1925.

[3] Loeb, L. B., *J. Franklin Inst.*, **201**, 286, 1926.

[4] Loeb, L. B., *Proc. Nat. Acad. Sci.*, **12**, 617 and 677, 1926.

[5] Wahlin, H. B., *Physic. Rev.*, **19**, 173, 1922.

[6] Loeb, L. B., *J. Franklin Inst.*, **196**, 537 and 771, 1923.

[7] Tyndall and Grindley, *Phil. Mag.*, **48**, 711, 1924.

[8] Wellisch, E. M., *Phil. Mag.*, **34**, 55, 1917.

[9] Loeb, L. B., *Physic. Rev.*, **17**, 89, 1921.

[10] Blanc, A., *J. Physique*, **7**, 825, 1908.

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*CURRENT DISTRIBUTION IN SUPRACONDUCTORS**

BY FRANCIS B. SILSBEE

BUREAU OF STANDARDS, WASHINGTON, D. C.

Read before the Academy April 26, 1927

W. Tuyn and H. Kamerlingh Onnes have published[1] an account of experiments carried out at Leiden on "The disturbance of supraconductivity by magnetic fields and currents." Part of this work constituted a rather crucial test of the hypothesis, suggested some years ago by the present author,[2] that the "critical current" observed in the early experiments on supraconductivity was merely that at which the magnetic field due to the current itself is equal to the critical magnetic field. In view of the ingenuity of the method and the carefulness of the experimental work, their results seem to deserve a somewhat more quantitative analysis than that given by the experimenters themselves.

The experiments here discussed were measurements of the potential difference between the ends of a slender tube of tin when currents were flowing both in the tube itself and in a wire stretched along its axis, but insulated from the tube. The specimen could be held at a temperature below that at which supraconductivity appears and the currents flowing in the tube and in the central wire could be adjusted independently to any desired values.

Let us assume that the tube is symmetrical and of homogeneous isotropic material and that, at the temperature of the experiment, it shows a definite critical magnetic field, H_c. By this is meant that material located where the field intensity exceeds H_c shows normal electrical resistivity while material located where the magnetic field is less than H_c shows the infinite conductivity exhibited by supraconductors cooled below their critical temperature. On these assumptions it is possible by a simple but rather laborious process to compute the potential difference between the ends of the tube for any given values of H_c and of the currents in the conductors.

These computations show that there will exist in the cross-section of the tube a number of zones in some of which the material will have normal resistivity while in others it may be supraconducting. In many cases the supraconducting layer shrinks to a current sheet of infinitesimal thickness but carrying a finite current.

In the experiments of March 12, 1924, the currents in the tube and in the wire were held constant while the temperature was varied through the critical range. In the first experiment current flowed in the outer tube only. In the second experiment the current in the inner wire was kept equal and opposite to that in the tube. The theory based on the above assumption indicates that the potential difference should finally vanish at the same temperature in both experiments, and that for a tube of the wall thickness used, the potential difference under conditions intermediate between full resistance and supraconduction should not differ in the two cases by more than 4 per cent of that corresponding to normal resistivity. The experiments showed no difference so great as 4 per cent between the two cases.

In the experiments of April 17, 1924, the temperature and the current in the tube were held constant, while the current in the inner wire was varied. For this procedure the analysis indicates that the graph of potential difference versus current in the inner wire would show a decrease to a minimum value followed by linear increase to the value corresponding to normal resistivity. For large values of current through the tube or high temperatures the curve should be V-shaped and the minimum potential difference might be considerable. For smaller currents or lower temperatures the curves should be U-shaped and the potential difference

should vanish over a certain range of current. Curves of both types were obtained in the experiments, and the slopes of the linear portions of the curves are in good quantitative agreement with the theoretical slopes.

It may, therefore, be concluded that the results of these experiments can be completely accounted for by the assumption of a critical magnetic field, without making use of the concept of critical current.

* Published by permission of the Director, Bureau of Standards, Department of Commerce. A more extended paper on this subject will appear as a scientific paper of the Bureau of Standards.

[1] *J. Franklin Inst.*, **201**, p. 379, April, 1926.

[2] *Bur. Standards Sci. Paper*, No. 307, 1917.

ON THE REFLECTION OF ELECTRONS FROM CRYSTAL LATTICES

By F. Zwicky*

Norman Bridge Laboratory of Physics, California Institute of Technology

Communicated May 31, 1927

(*a*) *Introduction.*—Davisson and Germer[1] have recently published their very interesting results on reflection of electrons from a single crystal of nickel. These results have been interpreted by analogy with the reflection of X-rays from crystals. This analogy, however, is not complete. The purpose of this short note is to point out the differences between the two phenomena. For the mathematical treatment use is made of the recent development of quantum mechanics (wave mechanics).

It is easy to see that a very important difference between the scattering of X-rays, as compared with the analogous phenomena for electrons, lies in the following fact. The scattering of slow electrons (of the order of 100 volt) is, crudely expressed, much more intense than that of X-rays. Indeed, one layer of atoms on the surface of a crystal may already deflect so considerable a part of an impinging beam of electrons that the effect can easily be observed. For ordinary X-ray scattering the effect produced by one layer is negligible and does not give an observable interference pattern. Only the coöperation of a large number of layers produces interference under the proper circumstances (Laue spots, Bragg reflection). We thus have the following difference. The interference pattern for X-rays is due to the action of a great number of lattice planes of a crystal, because of the small scattering coefficient of one layer. For the electrons, on the other hand, we have to expect that the action of a few layers on the

surface of the crystal already produces the whole effect. This is due to the high scattering coefficient of one lattice plane. From this point of view the pattern obtained by Davisson and Germer has been explained by Dr. Eckart.[2] There is also hope to provide in this way a reason for the hypothetical contraction of the lattice which Davisson and Germer have to introduce in order to establish the Bragg reflection law for their results.

In the following lines a derivation is given for the diffraction of an electron beam by a single lattice plane. A pattern is obtained similar to that for the reflection of light by a ruled crossed grating. The resolving power for a finite lattice is calculated. Finally it is shown that the reflecting power of a single plane is so large that it is not permissible to treat this case by analogy with X-rays. The interference pattern cannot be computed by assuming that the rays penetrate a great number of layers. On the contrary the whole phenomenon is produced by a few layers on the surface only.

The method which we apply is that given by M. Born[3] in a paper on periodic phenomena treated from the standpoint of wave mechanics. For its justification we refer to this paper.

The impinging beam of electrons of constant velocity, v, is represented by a wave function in space

$$\psi_0 = e^{ik(x\xi_0 + y\eta_0 + z\zeta_0)}. \qquad (1)$$

ξ_0, η_0, ζ_0 are the components of a unit vector indicating the direction of the beam. If m and E are the mass and the energy of an electron, λ the wave-length of the associated wave, then we have (de Broglie)

$$k = \frac{2\pi}{\lambda} = \frac{2\pi}{h}\sqrt{2mE} = 2\pi\frac{mv}{h} \qquad (2)$$

h = Plancks constant.

What we have to calculate then is the effect of a certain distribution of potential energy $V(x, y, z)$ in space on the primary beam as described by the equation

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0.$$

Born developed for this purpose the following method of approximation. Suppose

$$\psi = \psi_0 + \psi_1 + \psi_2 + \ldots\ldots$$

Then the successive approximations are given by

$$\psi_1(x, y, z) = -\frac{2\pi m}{h^2}\int dl' V(x', y', z')\psi_{i-1}(x', y', z')$$

$$\frac{e^{ik\sqrt{(x-x')^2+(y-y')^2+(z-z')^2}}}{\sqrt{(x-x^1)^2+(y-y')^2+(z-z')^2}}. \qquad (3)$$

The integral is to be taken over all space. The different function ψ_i satisfy these equations

$$\nabla^2\psi_0 + k^2\psi_0 = 0$$

$$\nabla^2\psi_i + k^2\psi_i = \frac{8\pi^2 m}{h^2} V.\psi_{i-1}. \qquad (4)$$

According to Born the intensity of the electron stream is measured by the expression $|\psi|^2$. The intensity of the scattered beam, in the first approximation, is given by $|\psi_1|^2$.

This method has been applied by Wentzel[4] to the case of scattering of α particles by nuclei. He obtained Rutherford's law as a first approximation.

(*b*) *Positions of the Maxima of Reflection.*—The potential energy of an electron in relation to a single lattice plane may generally be expressed by a double Fourier series in the two coördinates x and y for instance. As we only need the first approximation ψ_1, we may consider for simplicity the effect given by one member of this series only, without sacrifice of any essential features of the problem. This is indeed justified by the possibility of superposition of our solutions in the first approximation.[5] We, therefore, put

$$V(x, y, z) = A\cos\frac{2\pi mx}{l_1}\cos\frac{2\pi ny}{l_2}e^{-\alpha z^2-\beta(x^2+y^2)} \qquad (5)$$

where l_1 and l_2 indicate the spacings between the atoms. The factor $e^{-\alpha z^2}$ has to be introduced as a means of giving the layer the required thickness (of one atomic diameter, approximately). Adjusting the constant β in a proper manner means that we make use of a finite portion of the crystal only. In this way we shall obtain an estimate as to the resolving power of a definite experimental arrangement.

For a beam of electrons in the direction z, normal to surface, we assume the expression (1) mentioned above, namely

$$\psi_0 = e^{ik\zeta_{0z}}.$$

Assuming that the point (x, y, z) at which the reflected beam is observed is very distant we can write

$$\psi_1 = -\frac{2\pi m A e^{ikr}}{h^2 r}\int_{-\infty}^{+\infty}\int dx'dy'dz' \cos\frac{2\pi m x'}{l_1}$$

$$\cos\frac{2\pi n y'}{l_2}\exp[ik(\xi x' + \eta y' + \zeta z') - \beta(x'^2 + y'^2) - \alpha z'^2].$$

In this formula the following notations are used

$$r^2 = x^2 + y^2 + z^2$$

$$\xi = -\frac{x}{r} \qquad \eta = -\frac{y}{r} \qquad \zeta = -\frac{z}{r} + 1.$$

The integral is easily evaluated with the help of the following relations.

$$\int_{-\infty}^{+\infty} e^{ikz\zeta - \alpha z^2}\, dz = \sqrt{\frac{\pi}{\alpha}}\, e^{-\frac{k^2\zeta^2}{4\alpha}}.$$

The integrals with respect to x and y are similar, namely,

$$\int_{-\infty}^{+\infty} dx \cos\frac{2\pi m x}{l_1}\, e^{ik\xi x - \beta x^2}$$

$$= \frac{1}{2}\sqrt{\frac{\pi}{\beta}}\left[e^{-\frac{1}{4\beta}\left(\frac{2\pi m}{l_1} + k\xi\right)^2} + e^{-\frac{1}{4\beta}\left(\frac{2\pi m}{l_1} - k\xi\right)^2}\right] = \sqrt{\frac{\pi}{\beta}}\, F_m(\xi_m, \beta).$$

For the wave function of the scattered radiation, this expression then follows

$$\psi_1 = -\frac{2\pi^2\sqrt{\pi} A e^{ikr}}{h^2\beta\sqrt{\alpha}\, r} e^{-\frac{k^2\zeta^2}{4\alpha}} F_m(\xi,\beta) F_n(\eta, \beta). \qquad (6)$$

For an infinitely extended plane and an infinitely wide homogeneous beam of impinging electrons ($\beta = 0$) we thus get the following result. ψ_1 will be zero (in spite of the factor $1/\beta$) on account of the functions F_m and F_n becoming zero exponentially. There are, however, some exceptional cases, namely those when the brackets in the exponential functions are zero. In this case ψ_1 will be infinitely large. If the ξ and η satisfy the two equations

$$\begin{aligned} m\lambda &= \mp\xi_m l_1 \\ n\lambda &= \pm\eta_m l_2 \end{aligned} \qquad (7)$$

a maximum of intensity of the beam is obtained. These conditions for the appearance of maxima are analogous to those for diffraction of ordinary

light on a plane crossed grating. Giving m and n independently all integral values, the whole interference pattern is obtained.

(*c*) *Resolving Power.*—It is easy to see now what the conditions will be for a crystal of finite size. ($\beta \neq 0$.) For not too large values of β the maxima will still be in the same places. But they will not be of infinite intensity. They also will be spread out over the whole range of angles. The intensity falls off rapidly with $\Delta\xi = |\xi - \xi_m|$ increasing. The value for $\Delta\xi$ at which the intensity is diminished by a factor e^{-1} is readily obtained by the condition

$$\frac{k^2 \Delta\xi^2}{4\beta} = 1. \qquad (8)$$

Now in the actual experimental arrangement we have to put $\beta = 100$ cm.$^{-2}$ because this corresponds to a width of the primary beam of approximately 1 mm.

Assuming electrons with an energy corresponding to 100 volts we have approximately

$$k^2 = 3 \times 10^{17} \text{ cm.}^{-2}$$
$$\Delta\xi = 3.5 \times 1\ 0^{-8}.$$

It is seen by this that the resolving power is very large. The width of the lines which is found experimentally is of quite another order of magnitude. This may be partly accounted for by the imperfection of the apparatus, as the authors mention. It is, however, probable that a considerable width of the reflected electron beam is due to the imperfections of the crystal surfaces and to temperature agitation. This will be true especially because of the fact that probably only a few layers on the surface of the crystal coöperate to produce the whole effect. To prove this point we shall give now a rough estimate as to the scattering power of a single lattice plane.

(*d*) *Reflection Power of One Plane of Atoms.*—For simplicity we assume a distribution of potential energy non-periodic in x and y, such as

$$V = A \exp[-\beta(x^2 + y^2) - \alpha z^2].$$

This non-periodic term is present in the practical case too, due to a general image force, for instance. In the numerical application we will identify it for $z = 0$ with the work function φ

$$A = e\varphi \qquad e = 4,77 \cdot 10^{-10} \text{e.s.u.}$$

According to section (*b*) scattering will then only take place in the forward and in the backward direction. We have to put

$$m = 0 \qquad n = 0$$

which gives us (see formula 6)

$$\psi_1 = -\frac{2\pi^2\sqrt{\pi}mAe^{ikr}}{h^2\beta\sqrt{\alpha}r}\exp\left[-\frac{k^2}{4\beta}(\xi^2+\eta^2)-\frac{k^2\zeta^2}{4\alpha}\right].$$

The intensity of the scattered beam then, according to Born, is

$$|\psi_1|^2 = \frac{4\pi^5m^2A^2}{h^4\beta^2\alpha r^2}\exp\left[-\frac{k^2}{2\beta}(\xi^2+\eta^2)-\frac{k^2\zeta^2}{2\alpha}\right].$$

Denote the angle between the z axis and the direction of the reflected beam by θ. Then we have

$$\xi^2+\eta^2 = \sin^2\theta \qquad \zeta = 1-\cos\theta.$$

But $|\psi_1|^2$ is only appreciable for small values of θ. We may, therefore, use the following approximations

$$\xi^2+\eta^2 = \theta^2 \qquad \zeta^2 = \frac{\theta^4}{4} = 0$$

In order to get the total intensity I_1 of the beam scattered backwards we have to compute

$$I_1 = 2\pi\int_0^{\pi/2}|\psi_1|^2r^2\sin\theta d\theta.$$

This is with sufficient approximation for our purpose

$$I_1 = \frac{8\pi^6m^2A^2}{h^4\beta^2\alpha}\int_0^\infty e^{-\frac{k^2}{2\beta}\theta^2}\theta d\theta$$

$$I_1 = \frac{8\pi^6m^2A^2}{h^4\beta\alpha k^2}.$$

I_1 has to be compared with the intensity of the impinging beam integrated over the efficient part of the crystal, for which we have the expression

$$I_0 = \int_0^\infty|\psi_0|^2e^{-\beta r^2}2\pi r dr = 2\pi\int_0^\infty e^{-\beta r^2}r dr = \frac{\pi}{\beta}.$$

The desired ratio between the impinging and the scattered intensity is, therefore,

$$I_1/I_2 = \frac{8\pi^5m^2A^2}{\alpha k^2h^4}.$$

Substituting the expression for k^2 we obtain

$$I_1/I_0 = \frac{\pi^3 m A^2}{h^2 \alpha E}. \qquad (9)$$

The numerical value will be computed on the assumption that our single layer has a thickness of approximately 2×10^{-8} cm. This corresponds approximately to

$$\alpha = 0.25 \times 10^{16} \text{ cm.}^{-2}.$$

As mentioned we identify A with a potential energy corresponding to the work function ($\varphi = 5$ volts). The energy E of the impinging electrons may correspond to 100 volts. With these data we have approximately

$$A = e\varphi = 8.10^{-12} \text{ ergs}$$
$$I_1/I_0 = 0.11.$$

The scattering will be increased still considerably by the effect of the higher harmonics in $V(x, y, z)$. From this estimate it follows, then, that only a few layers of atoms on the surface of the crystal produce the diffraction phenomenon discovered by Davisson and Germer. The exact numerical value obtained for I_1/I_2 cannot be taken too seriously. Its magnitude indicates indeed that the approximation method applied is no longer rigorous enough for the potential energies in consideration. The order of magnitude, however, will not be affected by a more adequate calculation. The opacity of the crystal then seems to be established both from the experimental and the theoretical point of view. The crystal behaves in relation to electrons as a dispersive medium (with complex index of refraction) does in respect to light. The change of wave-length at the boundary of the crystal cannot be neglected. This is possibly the reason for the necessity of the contraction factor introduced by Davisson and Germer in order to establish Bragg's reflection law. An adequate theory for this contraction factor might be given by studying the effect of a thin sheet of a crystal on the impinging beam. It is easy to see that the first approximation of our theory would yield Bragg's law without a contraction factor. This factor only might be obtained by taking into account the second approximation or by solving the Schrödinger equation rigorously.

The experiments yield three anomalous maxima of reflection which do not seem to have any relation to the crystal structure. They are indeed independent of the azimuth. This suggests that they might be due to some adsorbed gas molecules, oxygen for instance. These adsorbed gases on the surface may also cause the diffuse continuous scattering over all the angles, especially at low velocities.

* Research Fellow, International Education Board.

[1] Davisson and Germer, *Nature*, 1927, April 16.

[2] C. Eckart, these PROCEEDINGS, **13**, 460, 1927. I am indebted to Dr. Eckart for private communication of his results.

[3] M. Born, *Zs. Physik*, **38**, 803, 1926.

[4] G. Wentzel, *Ibid*, **40**, p. 590.

[5] The general case will be treated elswhere by Dr. P. S. Epstein.

DISPLACEMENT OF CERTAIN MULTIPLETS AND MULTIPLE LEVELS FOR ELEMENTS IN THE FIRST LONG PERIOD[1]

BY R. C. GIBBS AND H. E. WHITE

DEPARTMENT OF PHYSICS, CORNELL UNIVERSITY

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In previous reports on the first long period of the periodic table we have shown how beautifully the regular and irregular doublet laws are found to hold not only for iso-electronic systems containing one[2] valence electron but also those containing two[3a] and three[3b] valence electrons. It has also been shown that the addition of 0, 1, 2 and 3 $3d$ electrons to the one-electron systems of K, Ca, Sc and Ti, respectively, cause not only a change in the multiplicity of the resultant terms but also a shift in radiated lines toward the longer wave-lengths. This regular displacement law of multiplets, as well as the irregular doublet law, has enabled us to locate approximately the position in the spectrum of certain characteristic multiplets of Cr III and Mn III, which multiplets arise from the electron transitions, $3d^3 4p$ to $3d^3 4s$ and $3d^4 4p$ to $3d^4 4s$, respectively. The data for these two multiplets are given in table 1. The regular doublet law in conjunction with Landé's interval rule was most effective in determining approximately the frequency differences between the terms of ${}^5F'_{1,2,3,4,5}$ $(3d^3 4s)$ and those of ${}^5G'_{2,3,4,5,6}$ $(3d^3 4p)$ for Cr III as well as between the terms of ${}^6D_{1,2,3,4,5}(3d^4 4s)$ and those of ${}^6F_{1,2,3,4,5,6}(3d^4 4p)$ for Mn III. These frequency intervals are so regular for both the initial and final states that the strong lines of each multiplet, i.e., the diagonal lines in table 1, were easily picked out before the lines were definitely identified by exact measurements.

Sufficient data is now available for elements in the first long period so that it is possible to extend the regular displacement law of multiplets, the nature of which has already been pointed out,[3b] through successively increasing iso-electronic systems as far as those of the Cu I, Zn II, etc., type. The wave-numbers given in table 2 and shown graphically in figure 1 were chosen in the following way. For the one-electron systems in the first column we have selected the strongest line of the principal doublet

$^2S_1 - {}^2P_2$ to represent the electron transition $4p$ to $4s$. In the two-electron systems (second column) a line, corresponding to this same electron transition, $4p$ to $4s$, in the presence of *one* $3d$ electron has been selected. This transition gives rise to the triad of multiplets $^3D_{1,2,3} - {}^3P_{0,1,2}$, $^3D_{1,2,3} -$

TABLE 1

$\lambda_{vac.}$

Cr III	$^5F_5'$	(318.4)	$^5F_4'$	(262.0)	$^5F_3'$	(201.0)	$^5F_2'$	(135.6)	$^5F_1'$
	100								
$^5G_6'$	2227.40								
	44895.4								
(503.7)									
	25		90						
$^5G_5'$	2252.67		2236.63						
	44391.7		44710.1						
(425.1)									
	2		25		80				
$^5G_4'$	2274.45		2258.10		2244.82				
	43966.6		44285.0		44547.0				
(346.4)									
			2		20		70		
$^5G_3'$			2275.90		2262.41		2252.17		
			43938.6		44200.6		44401.6		
(263.8)									
					2		20		60
$^5G_2'$					2276.00		2265.63		2258.69
					43936.8		44137.8		44273.4

Mn III	$^6D_5$	(296.6)	$^6D_4$	(241.3)	$^6D_3$	(179.5)	$^6D_2$	(132.2)	$^6D_1$
	100								
$^6F_6$	2069.72								
	48315.7								
(490.3)									
	50		80						
$^6F_5$	2090.94		2078.05						
	47825.4		48122.0						
(399.8)									
	5		50		70				
$^6F_4$	2108.57		2095.46		2084.92				
	47425.5		47722.2		47963.5				
(313.1)									
			5		50		60		
$^6F_3$			2109.30		2098.62		2090.74		
			47409.1		47650.4		47829.9		
(225.8)									
					6		50		50
$^6F_2$					2108.61		2100.66		2094.84
					47424.6		47604.1		47736.3
(158.0)									
							?		40
$^6F_1$							2107.66		2101.80
							47446.0		47578.3

TABLE 2

REGULAR DISPLACEMENT OF MULTIPLETS BY SUCCESSIVE ADDITION OF "d" ELECTRONS

DOUBLETS	TRIPLETS	QUARTETS	QUINTETS	SEXTETS	SEPTETS
$s-p$					
$^2S_1-{}^2F_2$	$ds-dp$				
K I					
13043					
(12371)	$^3D_3-{}^3F_4$	QUARTETS			
Ca II	Ca I	d^2s-d^2p			
25414 9888	15526				
(11626)	(12138)	$^4F_5'-{}^4G_6'$	QUINTETS		
Sc III	Sc II	Sc I	d^3s-d^3p		
37040 9376	27664	10038 17626			
(11311)	(12070)	(12221)	$^5F_5'-{}^5G_6'$	SEXTETS	
Ti IV	Ti III	Ti II	Ti I	d^4s-d^4p	
48351 8617	39734	9887 29847	9779 20068		
(11164)	(11837)	(12316)	(12253)	$^6D_5-{}^6F_6$	SEPTETS
V V	V IV	V III	V II	V I	d^5s-d^5p
59515 7944	51571	9408 42163	9842 32321	9492 22829	
(11020)	(11995)	(12181)	(12574)	(12426)	$^7S_3-{}^7P_4$
Cr VI	Cr V	Cr IV	Cr III	Cr II	Cr I
70535 6969	63566	9222 54344	9449 44895	9640 35255	11756 23499
(10843)				(13059)	(15308)
Mn VII	Mn VI	Mn V	Mn IV	Mn III	Mn II
81378				48316	38807

SEPTETS	SEXTETS	QUINTETS	QUARTETS	TRIPLETS	DOUBLETS
d^6s-d^6p					
$^7S_3-{}^7P_4$	$^6D_5-{}^6F_6$				
Cr I					
23499					
(15308)		QUINTETS			
Mn II	Mn I	d^7s-d^7p			
38807 12547	26260				
	(15708)	$^5F_5'-{}^5G_6'$	QUARTETS		
	Fe II	Fe I	d^8s-d^8p		
	41968	14052 27916			
		(15812)	$^4F_5'-{}^4G_6'$	TRIPLETS	
		Co II	Co I	d^9s-d^9p	
		43728	14780 28948		
			(16155)	$^3D_3-{}^3F_4$	DOUBLETS
			Ni II	Ni I	$d^{10}s-{}^{10}dp$
			45103	15827 29276	
				(17528)	$^2S_1-{}^2P_2$
				Cu II	Cu I
				46804	16020 30784
					(18571)
					Zn II
					49355

$^3D'_{1,2,3}$, $^3D_{1,2,3}-{}^3F_{2,3,4}$ and the triad of singlets $^1D_2-{}^1P_1$, $^1D_2-{}^1D_2'$, $^1D_2-{}^1F_3$, from which the strongest line $^3D_3-{}^3F_4$ has been taken to represent

that electron transition. For the three electron systems this same electron transition $4p$ to $4s$ in the presence of *two* $3d$ electrons gives rise to triads of doublets and quartets. Again the strongest line in these triads ${}^4F_5' - {}^4G_6'$, corresponding to two terms involving the largest R, L and J values, has been taken to represent the transition $3d^24p$ to $3d^24s$. In like manner for the systems containing four, five, six, etc., valence electrons we have taken the strongest line resulting from the electron transition $4p$ to $4s$ in the presence of three, four, five, etc., $3d$ electrons, respectively. It will be noted in the first half of table 2 or figure 1 that the multiplicity, R, of

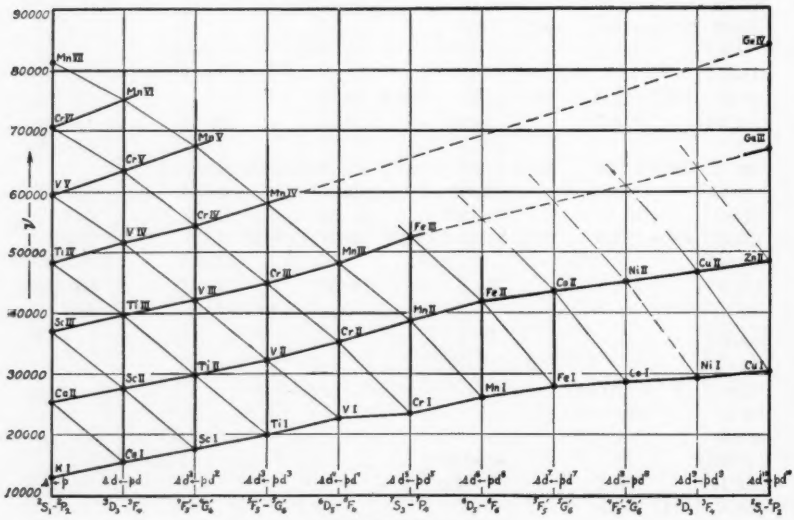

FIGURE 1

Regular displacement of multiplets.

these terms, starting with doublets in K I, Ca II, etc., increases until septets are reached in Cr I, Mn II, etc., then decreases again in the second half to doublets in Cu I, Zn II, etc. The L and J values of the terms, however, show a maximum at the center of each half of the table and a minimum in the center and at both ends of the entire table. The irregular doublet law, which applies to transitions involving the same total quantum numbers but different azimuthal quantum numbers, not only requires a linear progression of ν with atomic number but also indicates that the term values if plotted on the Moseley type of diagram should yield very nearly parallel lines. This relation we have found holds not only for doublets[2] but for certain sequences of triplets[3a] and quartets.[3b] Since the almost equal intervals on any vertical scale of figure 1 correspond to regularities just mentioned for the terms on the Moseley type of diagram, it is reasonable

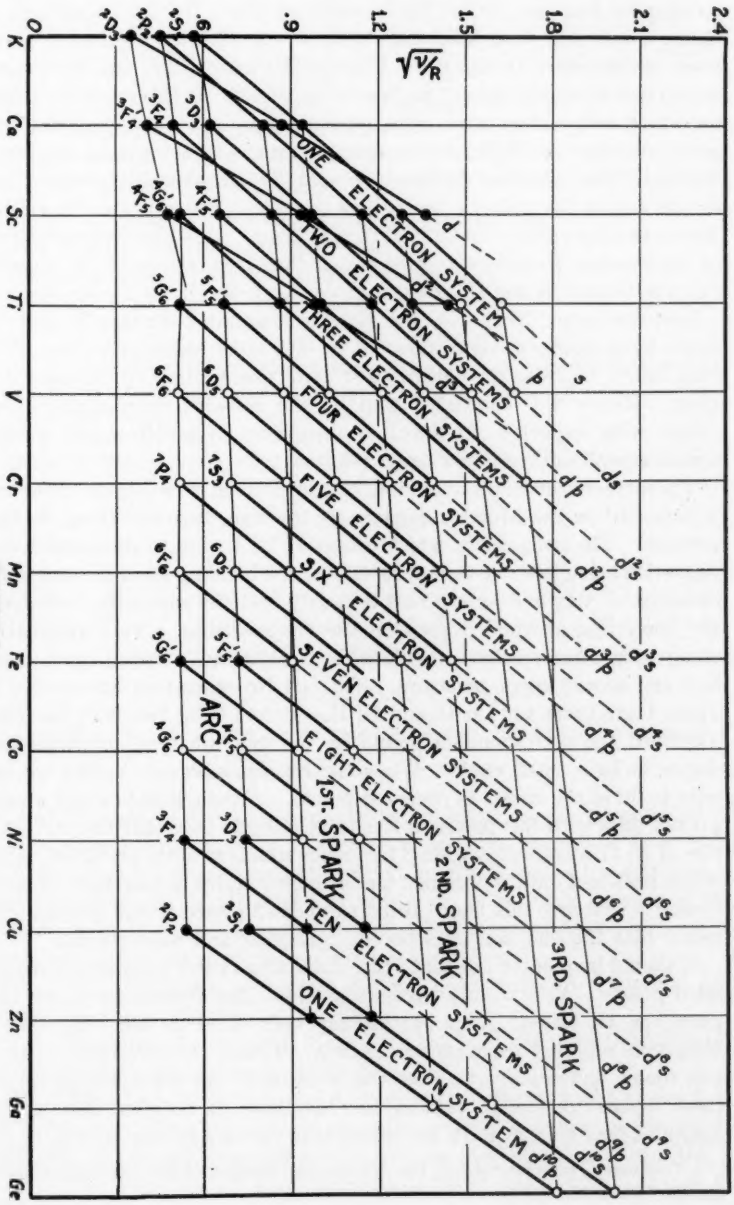

FIGURE 2

Regular displacement of multiple levels.

to suppose that the almost equal intervals down the light diagonals of figure 1 will also show some regularity on the Moseley diagram in going from one sequence to another. Making this assumption and using term values now available, figure 2 has been constructed. In this figure the points for which term values have been determined by other investigators from series relations are indicated by dots. Terms which we have computed by use of the irregular doublet law and this regular displacement law for the rest of the radiated lines given in table 1, are indicated by circles. The term values used to obtain figure 2 are in cm.$^{-1}$ and have values referred to the limiting frequency toward which that term converges in a series, e.g., the terms $^3D_3$ and $^3F_4$ (ds and dp) in Ca I, Sc II, Ti III, etc., have as a limit the term $^2D_3(d)$. On the Moseley diagram both the $^3D_3$ and $^3F_4$ terms form nearly straight lines. The $^2D_3$ terms (taken with respect to their limits, $^1S_0$) also show nearly a straight line relation on the same diagram. Hence it is concluded that on the Moseley diagram any term (taken with respect to its limit) in a sequence of iso-electronic systems should reveal very nearly a linear relation.

The increased strength of binding of a $3d$ electron over a $4p$ or $4s$ electron is indicated on the Moseley diagram for the one-, two- and three-electron systems. The irregularity which occurs at Cr I (due to the normal configuration being $3d^54s$ instead of $3d^44s^2$) for the building up of the successive elements of this first long period is clearly brought out in the first figure the lower line of which represents the arc spectrum. This irregularity along with other smaller irregularities, is somewhat "ironed out" in the first and second spark spectrum. The last two points we have added to figure 1 are those for Cu II and Ni II. Before these two lines had been identified the corresponding points on the diagram were predicted and drawn in by a small circle. When the two lines became known we had only to fill in the circles as observed points. Although one cannot always predict lines with this precision it is interesting to note that the $^4F_5' - {}^4G_6'$ line of Ni II was found within 3 frequency numbers of its predicted value. When sufficient data is obtained for the higher states of ionization of these elements enabling this figure to be extended upward it will probably be found that the diagonal lines become smoother and more regular.

It should be pointed out that figure 2 contains a good many semi-extrapolated points. As new data becomes available the correctness of the diagram can be tested. This has already been done in one case. When Shenstone reported the term values of the $^3F_4$ and $^3D_3$ levels for Cu II, it was found unnecessary to alter the location of the predicted points for these levels. Sufficient data is now available to indicate that similar diagrams may be drawn for the elements in the second long period.

[1] This paper was presented at the Washington Meeting of the American Physical Society, April 23, 1927.

[2] Gibbs, R. C., and White, H. E., these PROCEEDINGS, **12**, 448, 598, 675, 1926.
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ENERGY RELATIONSHIPS AND IONIZATION POTENTIALS OF ATOMS OF THE FIRST ROW OF THE PERIODIC TABLE IN ALL STAGES OF IONIZATION

BY R. A. MILLIKAN AND I. S. BOWEN

NORMAN BRIDGE LABORATORY OF PHYSICS, CALIFORNIA INSTITUTE OF TECHNOLOGY

Read before the Academy April 25, 1927

With the aid of the four agencies listed below we have been able to complete the identification of all of the extreme ultra-violet lines (λ = 2000 A to λ = 200 A) of any strength emitted by the atoms of the first row of the periodic table in all stages of stripping. *The main features of the spectra of these atoms may then be considered as now determined.* The agencies used in these identifications are the following:

(1) The Rydberg-Ritz formula handed down from the empirical age in spectroscopy preceding 1913 (Bohr).

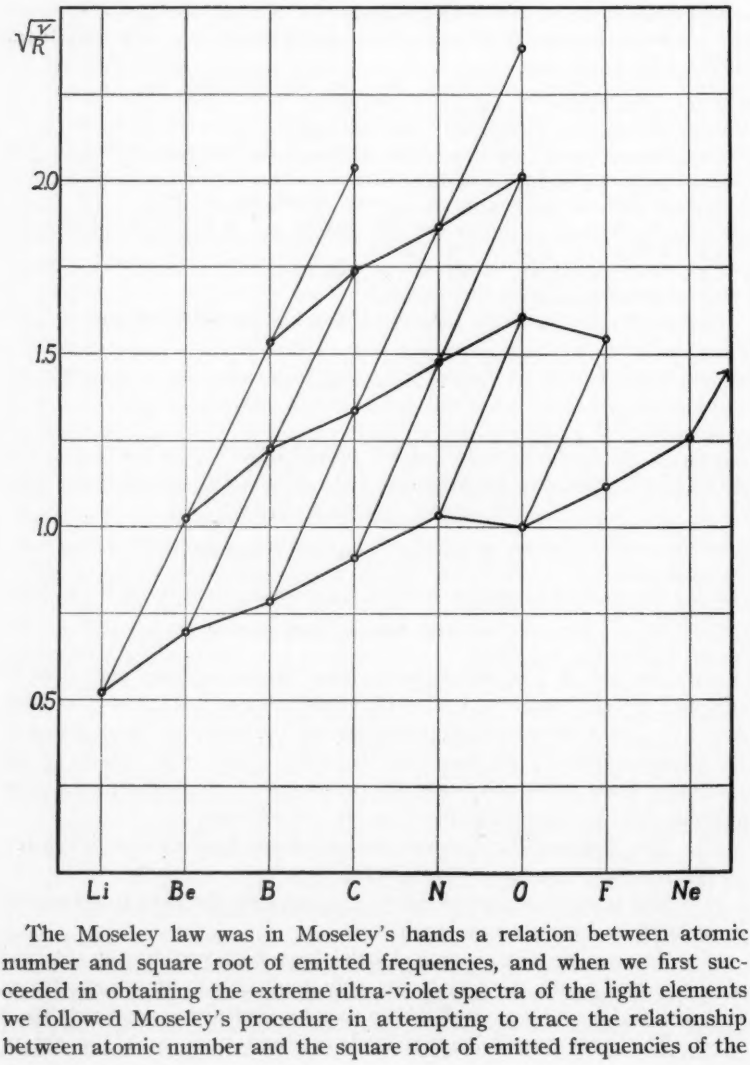
(2) The Bohr theory which since 1913 has been the most fundamental instrument of spectroscopic prediction.

(3) The regular and irregular doublet laws discovered first in the field of X-rays and found by us to be not only applicable to optical spectra as well, but to be very powerful aids in making identifications of spectra.

(4) The new Russell-Pauli-Heisenberg-Hund rules with the aid of

which *the structure* of the spectra, even of the most complex electron configurations, can be completely foretold.

The completion of these identifications now makes possible the most general representation of the extension of diagrams of the Moseley type into the region of low atomic numbers (see Fig. 1).



The Moseley law was in Moseley's hands a relation between atomic number and square root of emitted frequencies, and when we first succeeded in obtaining the extreme ultra-violet spectra of the light elements we followed Moseley's procedure in attempting to trace the relationship between atomic number and the square root of emitted frequencies of the

L series down to neon, and then with the aid of a line which now departed largely from linearity from neon down to hydrogen.[1]

We have herein, however, adopted the more correct and the more significant procedure—one also recently followed by most other authors—of presenting as the Moseley diagram the relation between atomic number and the square root of the frequencies of the *energy levels* rather than of any series of emitted lines.

Figure 1 presents, then, in such a general form the extension of the Moseley diagram from neon down through lithium.

The first straight line to the left is the Moseley diagram for stripped atoms, i.e., for one-electron systems. The plotted points are the energies, spectroscopically determined, necessary to remove an electron from the $2p$ orbit of the stripped atoms from lithium through carbon. The corresponding energy for stripped nitrogen, oxygen and fluorine can, of course, be obtained with much precision by simply extending upward the straight line in question.

The second line from the left gives, similarly, the observed energies necessary to remove an electron from the $2p$ orbit of a two-electron system from beryllium to carbon, and it makes possible, by a similar extrapolation, the determination of the corresponding energies in two-electron nitrogen, oxygen and fluorine.

Similarly, the third line from the left gives the corresponding energies for a three-electron system; and so on for four-, five- and six-electron systems. For seven- and eight-electron systems the graph shows but one point for each, but even here the direction of the Moseley lines might be obtained with considerable accuracy by simply paralleling the other Moseley lines farther to the left in the diagram.

The irregular line connecting the lowest points in the diagram represents at each point the energy necessary to detach a p electron from a *neutral* atom. *This line, representing a sequence of corresponding energy levels in neutral atoms rather than a sequence of emitted frequencies, has perhaps the best claim of any of the lines shown, to be regarded as the extension of the Moseley diagram from neon down to lithium.* From neon up to uranium this line of energy levels runs continuously with little change in slope and always in the approximate direction of the arrow shown starting obliquely upward from neon.

From a somewhat broader point of view the whole diagram is but the graphical representation of the extension of the Moseley graph to the atoms below neon.

In table 1 are presented the most important ionizing potentials, spectroscopically computed, of the atoms of the first row in a large number of stages of ionization. The potentials that have bracketed numbers beneath them are among those that are of particular significance for the

determination of stellar temperatures. Indeed, the bracketed numbers represent ionizing potentials which have heretofore been merely estimated, sometimes too with very considerable errors, as is seen from their values, from other means of obtaining stellar temperatures.[2]

IONIZATION POTENTIALS

Li	[3] 5.371			
Be	[7] 9.50	[4]18.141		
B	[8] 8.34	[7]24.2	[5]37.786	
C	[8]11.3	[8]24.289	[7]45.5 (45)	[6]64.23
N	[9]14.494	[8]29.56 (24)	[8]47.2 (45)	
O	[10]13.565	[8]34.999 (32)	[8]54.8 (45)	[8]77.0
F	[8]16.9	[8]82.3		
Ne	[11]21.482			

In considering ionization potentials it should not be overlooked that *unless there has been careful definition the term ionizing potential has no definite meaning at all.* Thus the normal oxygen atom has two electrons in s orbits and four in p orbits, and this configuration is, therefore, designated as the s^2p^4 configuration; but this configuration has triplet P, singlet D and singlet S terms, which correspond to five different orientations of the orbits and the spins of the four p electrons. When one of these p electrons is removed, the atom, now an ion, having left two s and three p electrons, may in its turn exist in any one of five different states, namely a quartet S, a doublet P, and a doublet D, *so that the atom can be ionized in twenty-five different ways each of which requires a slightly different energy and hence represents a different ionization potential from all the others.* "Ionization potential," therefore, has no definite significance, unless it is defined, for example, as the energy corresponding to the passage from the most stable state of the atom to the most stable state of the ion. It is this definition that has been used in the calculation of the foregoing table.

All of the foregoing investigations have been carried out with the aid of funds provided by the Carnegie Corporation of New York and administered by the Carnegie Institution of Washington.

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[11] Lyman and Saunders, *Proc. Nat. Acad. Sci.*, **12**, 92, 1926.

POLARIZATION OF LIGHT REFLECTED FROM ROUGH SURFACES WITH SPECIAL REFERENCE TO LIGHT REFLECTED BY THE MOON

BY F. E. WRIGHT

GEOPHYSICAL LABORATORY, WASHINGTON, D. C.

Read before the Academy April 25, 1927

The human race has always been interested in the moon and in its influence on living things; and has speculated much about its origin, its surface features and its course through the heavens. Notwithstanding this long-continued interest, however, we do not yet know what the materials are that we see exposed at its surface, nor do we know definitely how any one of its many surface features was formed.

This problem appealed to Dr. John C. Merriam, President of the Carnegie Institution of Washington, as one that might be attacked most effectively by a group of men from the fields of astrophysics and geology; he accordingly appointed a committee of members within the Institution interested in these sciences to study the surface features of the moon with special reference to the factors that were active in producing the observed surface forms.

In approaching this task as one of the geologist members of this group the writer has felt that the first step to be taken is to find out, if possible, what substances are exposed at the moon's surface before the more difficult problem of the origin of its surface features is considered seriously. Unfortunately, we cannot make an excursion to the moon and learn at first hand what its materials are. Our only approach to the moon at present is through the aid of the reflected sun's rays. These rays reach us a little over a second and a quarter after they leave the moon and can tell us much about its surface materials by reason of the effects these produce on the sun's rays on reflection. By comparing the reflected sun's rays with the direct sun's rays we can ascertain what changes are produced on reflection at the moon's surface; then by comparing these changes with the effects produced on reflection by terrestrial materials, we may be able to form some idea of the composition of the lunar surface materials.

The effects produced on reflection are of two kinds: (1) changes in the relative intensities of different wave-lengths, from the infra-red through

the visible spectrum into the ultra-violet. Also changes in the total amount of light reflected at different angles of incidence. (2) Degree of polarization of the reflected rays. In this paper the polarization phenomena only are considered.

A beam of light on reflection from a polished plate is polarized to a certain extent, the amount depending for a given substance on its refringence and on the angle of incidence. Light is said to be plane polarized when its vibrations take place in one plane. Brewster showed in 1811 that when the reflected ray is perpendicular to the refracted ray, the amount of plane polarization is a maximum; this angle is called Brewster's angle. The general theory of the polarization of light reflected from crystal plates was worked out by Fresnel, F. E. Neumann, MacCullagh, Drude, and others.

The amount of polarized light contained in a beam of light can be ascertained by different methods, but most readily by use of a polarization photometer of which there are several types available. In all of these types, however, the object is not imaged in the photometric field; this is a serious drawback when one wishes to make measurements on details of the moon. To meet this difficulty a new type of polarization photometer has been devised[1] and has been found, when used as an eyepiece on the 12-inch refracting telescope at the U. S. Naval Observatory, to serve its purpose well. Through the courtesy of Professor Asaph Hall of the Naval Observatory the writer has been allowed to use the 12-inch telescope for these measurements. The polarization of the rays reflected by the moon at its different phases is now being studied by the writer with the aid of the new eyepiece. A number of measurements have already been made; but many more are planned during the next few months. Measurements have been made at different phases of the moon and at no time have the angles required to produce a photometric match exceeded 2° to 4° from the diagonal position of the analyzer. This small angle signifies that the amount of polarized light in the moon's rays does not exceed 15 to 25 per cent. At new moon and at full moon practically none of the reflected light is polarized; the greatest amount of polarization is obtained about the end of the first and third quarters of the moon.

Measurements were also made on terrestrial materials for comparison. The polarization photometer eyepiece was converted temporarily into a telescope by the addition of a small objective mounted in an extension tube. The specimens were illuminated by the aid of parallel rays from a lantern and the angle between the incident and the reflected rays entering the telescope was carefully measured. For each substance the amount of polarized light in the reflected beam was ascertained for the following angles of incidence: 15°, 30°, 45°, 60°, 75°. The results for some of the substances measured are presented in figures 1 to 3. In these diagrams

the abscissae are the angles of incidence; the ordinates, the values of the angular settings of the photometer; also the percentage amounts of polarized light corresponding to these angles.

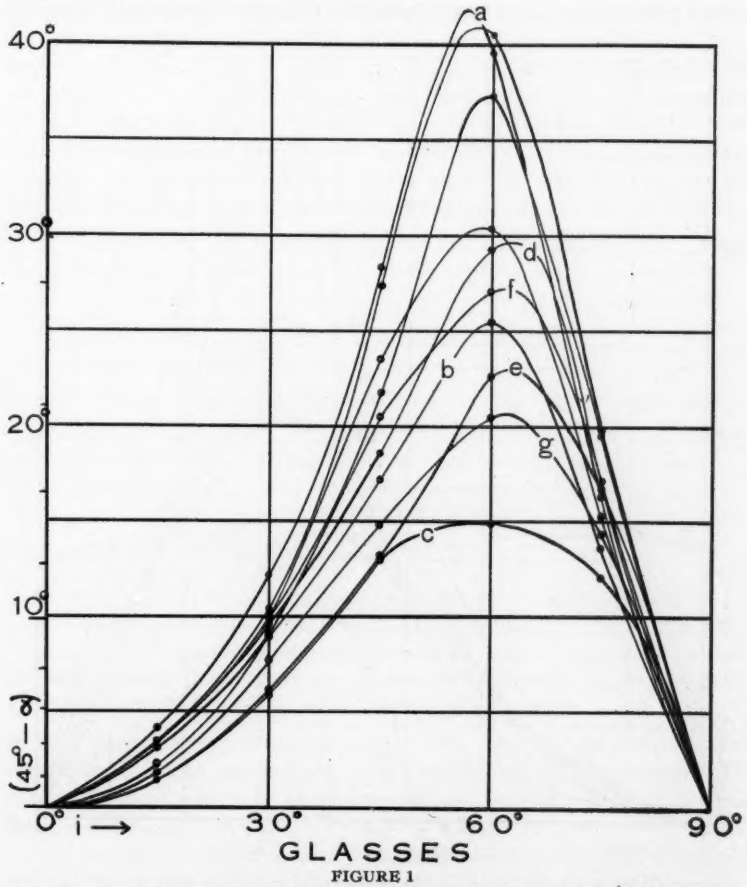

FIGURE 1

These curves show the observed amounts of polarization produced on the reflection of a plane parallel beam of white light incident at different angles i on plates of polished and ground plates of glass. The ordinates are the position angles of the analyzer on the polarization photometer; the small, unevenly spaced lines indicate the percentages, at 10 per cent intervals, of polarized light contained in the reflected beam. Curves a, b and c show the amounts of polarization in beams incident at different angles i on: (a) a polished plate of silica glass; (b) a finely ground surface (beveled finish) and (c) a surface ground with medium emery. Curves d, e, f, g illustrate similar observations on fine and coarsely ground surfaces of flint glass; in each case the amount of polarization increases as the glass surface approaches the polished state.

Beginning with optical glasses of known refractive indices we find that a polished surface of silica glass polarizes the light most completely as shown by the upper curve (*a*) of figure 1. The values obtained from a slab of silica glass ground finely but not polished are lower than those for

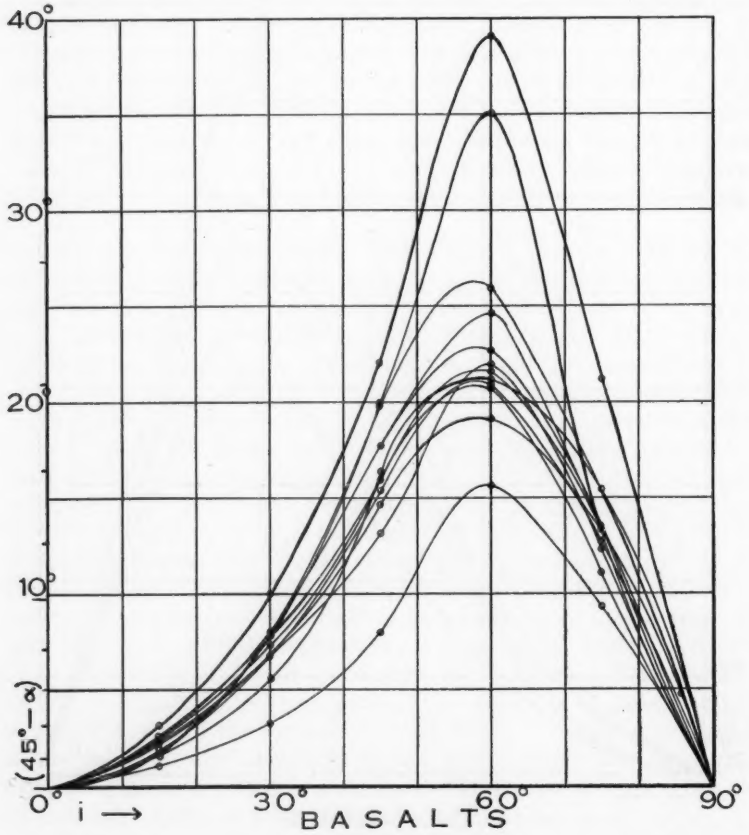

FIGURE 2

Curves similar to the curves of Fig. 1 sand showing the amounts of polarization, for different angles of incidence, in light reflected by rough fracture surfaces of basalt specimens from different parts of the world.

the polished plate (curve *b*); while for the coarsely ground plate still lower values are obtained (curve *c*). For dense flint glasses the maximum polarization occurs at a larger angle of incidence than that for silica glass (curves *d*, *e*, *f*, *g*). Polished and ground surfaces of obsidians, pitchstones, felsites and other shiny rocks showed results similar to those obtained

for the glasses. For basalts from different parts of the world the results are presented in figure 2. The curves differ somewhat from specimen to specimen but in no case are low percentages of polarization found for the intermediate angles of incidence. The polarization effects for a host of other basic rocks, such as diabase, peridotite, serpentine, magnetite, monchiquite, tephrite, etc., are similar to those for basalt. For basalt powders of different degrees of fineness the amount of polarization falls off with the degree of fineness; but even for powders finer than 200 mesh the polarization effects excede those produced by the moon. Measurements on meteorites, especially stony meteorites loaned to the writer through the courtesy of Professor G. P. Merrill of the U. S. National Museum, show that the iron meteorites polarize the light strongly; light

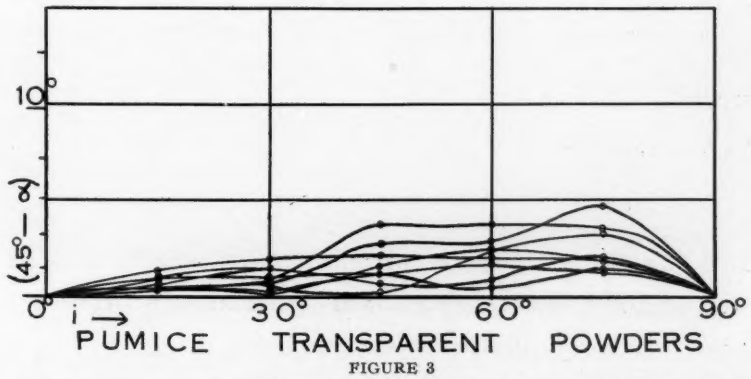

FIGURE 3

Curves showing observed amounts of polarization in plane parallel beams of light reflected by pumice, quartz porphyry, limestone and the powders of different transparent substances, such as quartz, sulphur, siliceous sinter and glass.

colored stony meteorites polarize less, dark stony meteorites slightly more than the iron meteorites. Some of the soft, rather fine-grained meteorites show relatively small polarization, but still more than does the moon surface.

Pumice, powders of transparent materials such as glasses, salts, marble, sulphur, yield low polarization angles like those observed on the moon. Granites, sandstones and similar rocks show, on fracture surfaces, angles appreciably greater than those observed on the moon. But in powder form these angles are smaller, and of the right order of magnitude. Coal, lampblack and other opaque substances show high polarization angles. Ice on fracture surfaces shows high angles. Snow would probably show low angles. It is characteristic of many powder preparations that the polarization angle increases relatively as the angle of incidence increases up to 75° and over. This characteristic may aid us in determining how

much of the moon's surface material is in the form of fine powder. The total amounts of light reflected at different angles of incidence will also aid in interpreting the surface conditions on the moon.

The results thus far obtained indicate clearly that there are not exposed directly on the moon's surface dark rocks low in silica, such as basalts, peridotites, serpentines, gabbros, etc. Nor are there masses of iron, such as one might expect from meteorites; nor are there any large ice masses nor glassy obsidians, nor are there powders of basic rocks. The indications, so far as they go, point to pumiceous substances high in silica, to powders of transparent substances and to quartz porphyries and possibly to trachytes and granites as the materials we see at the moon's surface. This is what we might anticipate when we consider the density of the moon, 3.4 as against 5.5 for the earth. We should not expect to find, exposed over large areas of the surface of the moon, basalts and other basic rocks with densities of 3.0, approaching closely to the density of the moon itself.

[1] F. E. Wright, "A Polarization Photometer Eyepiece," *J. Opt. Soc. Amer. Rev. Sci. Inst.*, **14**, 339–341.

THE TRAILS OF TWO PERIODICALLY FLICKERING METEORS

By Willard J. Fisher, Esther L. Wurl and Marjorie S. Desmond

Harvard College Observatory

Communicated June 2, 1927

During the search of Harvard Observatory plates, instituted for the discovery of meteor photographs, under the auspices of the J. Lawrence Smith Fund of the National Academy of Sciences, certain meteor trails have been found which indicate a recurrent change in brilliancy during flight. On two of these, selected as quite remarkable, we have spent some time, during the academic year 1926–27, in the endeavor to ascertain whether the fluctuations in brightness could be explained by some periodically acting cause.

The two trails were photographed at Arequipa, on 8 × 10 inch plates, with a Cooke lens of 13-inch focus, worked at $f/11$. The plates in question are, AM 1582, September 27, 1902, centered on 1^h00^m $-45°$, 473 minutes' exposure (studied by Miss Wurl); and AM 6090, May 8, 1909, centered on 9^h00^m $-60°$, 130 minutes' exposure (studied by Miss Desmond). Figure 1 is an enlargement, × 2, of a part of AM 6090.

The focal length of the lens was first determined by measurements of a star triangle which included the plate center on each plate and gave three

values for each plate; the general mean is 33.56 cm. Details of the reduction are deferred to another paper.

The trails were then examined for straightness, i.e., to see whether they represent great circles on the sky. A pair of stars is selected, with the trail passing between the stars and the star-chord making a favorable angle with the trail. The distance from each star to the intersection of trail and star-chord is measured several times with a $^1/_5$ mm. glass scale (by Gaertner), estimating tenths of fifths where possible. Also the distance from the center of the plate, of each star used, is measured with a photographic copy of a 16-cm. glass scale in millimeters (also by Gaertner), estimating tenths of millimeters. A photographer's focussing glass was used in all measurements.

FIGURE 1
Meteor trail on Harvard (Arequipa) Plate AM 6090.

In theory, the "plate center" is the foot of a perpendicular let fall from the rear principal point of the lens to the plane of the plate. In practice the intersection of the diagonals of the plate, marked with an ink dot, is used for this ideal point. The cameras are so constructed that the error is small; and the reduction process is one of interpolation between known stars near together, so that an approximate plate center serves all purposes. Details of reduction are deferred.

Six pairs of stars were used with each trail. The points found were:

AM 1582; (1) $1^h16.74^m$ $-45°40'$; (2) $1^h24.29^m$ $-47°23.6'$; (3) $1^h44.83^m$ $-50°59.0'$; (4) $1^h53.56^m$ $-52°06.7'$; (5) $2^h24.74^m$ $-55°58.6'$; (6) $3^h03.92^m$ $-59°20.2'$.

Positions from Uranometria Argentina, equinox 1875, precision 1^s and 0.1′, checked by the meridian circle at Còrdoba.

AM 6090; (1) 6^h05^m 38.1^s $-69°14.9'$; (2) $6^h22^m20.5^s$ $-71°06.6'$; (3) $7^h21^m51.8^s$ $-75°25.7'$; (4) $8^h24^m22.2^s$ $-77°34.3'$; (5) $8^h50^m07.6^s$ $-78°00.2'$; (6) $10^h36^m08.0^s$ $-78°22.5'$.

Positions from Cape Photographic Durchmusterung, equinox 1875, accuracy stated to be about that of the Bonner Durchmusterung, 1^s (on equator) and 1′, or better.

The points for each trail were tested by finding the pole of a great circle, through points (1) and (6) for AM 1582, points (1) and (5) for AM 6090

and computing great circle arcs from the pole to the other points on each trail. The results are:

AM 1582; (2) 90° + 0.83′; (3) 90° + 0.88′; (4) 90° − 0.17′; (5) 90° + 0.11′.
AM 6090; (2) 90° + 0.90′; (3) 90° − 0.98′; (4) 90° + 0.43′; (6) 90° + 0.26′.

The differences from 90° are such as can be reasonably explained by errors of catalogue positions, errors of measurement and errors in final places of logarithms. Hence the two trails may be taken to be projections of great circles, and presumably of straight paths.

It is interesting that measured meteor trails are, in general, nearly straight, indicating that the *luminous* part of the air-path is also nearly straight.

The study of the flickering brilliancy of each meteor was then taken up.

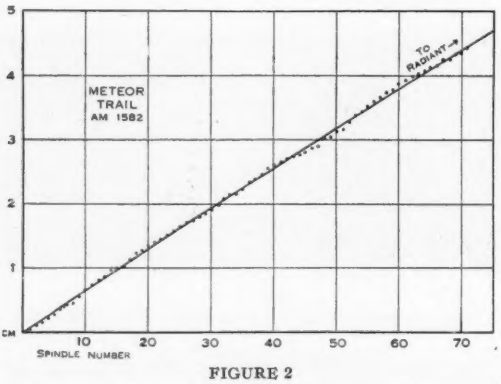

FIGURE 2

Flicker maxima, meteor trail on Harvard (Arequipa) Plate AM 1582.

In the following, the word *spindle* has been adopted as a name for an enlargement of the trail due to increased brightness of the image traveling along the film. The general effect is that of spindle-shaped beads strung on a thread; so the word spindle describes the appearance on the plate and is otherwise entirely non-commital. It remains a useful term, whatever the theory of the causes of flicker.

The plate was marked on the glass side with a grease pencil streak parallel to the trail and slightly separated from it. On this a mark was made opposite the widest part of each spindle and the marks were grouped in fives (this was simply for convenience in counting). A scratch was made on the film near one end of the trail, in line with the stars of a pair already previously used, so that the intersection of the scratch with the trail represented a point on the trail of known celestial position. Any slight error could be (and was) determined by a supplementary measurement; but it turned out that no correction would be useful. The film side

of the plate was then placed down upon the film side of a large (14 × 17 inch) plate on which was a contact photograph of the 16 cm. glass scale already described. The trail and the ends of the scale divisions were adjusted conveniently, and the scale reading for the scratch point of the trail and for the maximum point of each spindle was estimated to 0.1 mm. This was done three times, with complete resetting of the scale between series.

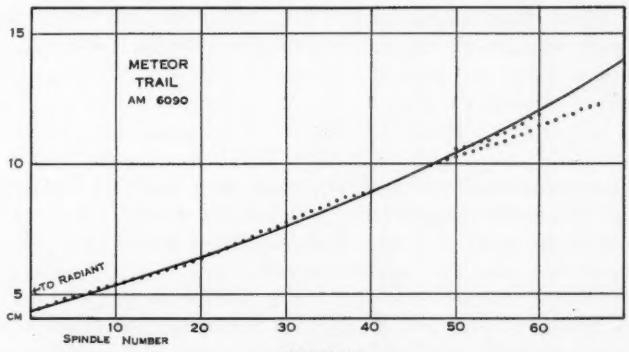

FIGURE 3

Flicker maxima, meteor trail on Harvard (Arequipa) Plate AM 6090.

The interval between the scratch point and each spindle maximum was found for each series, and the results averaged for each spindle. These average values were plotted as ordinates, λ (Figs. 2 and 3), and the counted (ordinal) spindle numbers as abscissas, n. In each case a generally curved and somewhat wavy row of points was formed.

Inasmuch as the meteor path in space is, in general, not parallel to the plate plane, these plotted points cannot be interpreted by comparison with a straight line. A line for comparison was derived with the aid of the following theory.

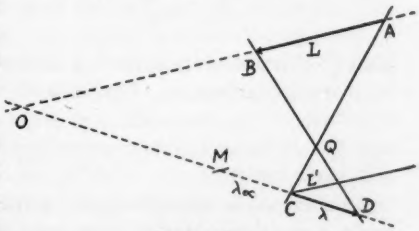

FIGURE 4

In figure 4, AB is part of the actual path of a meteor, supposed straight, the direction of motion being from A toward B; CD is the trail formed on a plate by a lens at Q, the image moving from C toward D. AB and DC prolonged intersect at O. (While CD is in the plane of the plate, AB is not, in general, parallel to that plane.) Let C be a point of the trail taken arbitrarily as an origin of measurement, say the scratched point above; then A is equally a point

fixed in the path, and the triangle ACO is a fixed plane triangle cut by a variable transversal BD. Then

$$AB \times CQ \times OD = OB \times AQ \times CD.$$

Represent AB by L, CO by c, AO by a, QA by A, QC by C, CD by λ, and adopt as rule of signs that toward O is positive, from either A or D, etc. Let M, somewhere in CO, be the projection of the radiant, the perspective vanishing point of AB prolonged backward. (M may be on or off the actual plate.) Also call CM $\lambda\infty$. Draw through C a line parallel to the path, and let the length L' be cut off on this by C and QD. Then, reducing,

$$1/\lambda + \frac{a/c}{L'} = 1/\lambda\infty. \qquad (1)$$

Also, $a/c = \sin QCO/\sin e$, in which e is the elongation of A from the radiant, as seen from Q. If the path AB be divided into *equal* parts in any way, let $L = \alpha + n\beta$. Then also $L' = \alpha' + n\beta'$. In these n is integral, but positive, negative or zero.

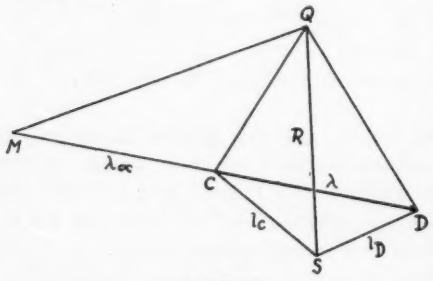

FIGURE 5

The angle QCO can be determined by plate measurements, with sufficiently good approximation, thus:

In figure 5 let Q be the lens, $QS = R$, the perpendicular let fall from Q to the plate, C, D, O, λ, $\lambda\infty$ as before, l_C and l_D the distances from S, the foot of the perpendicular, in the plane of the plate, to C and D. R being the focal length of the lens, QCO is found by plane trigonometry, and, given e, $\lambda\infty$ is also found by plane trigonometry. Equation (1) becomes

$$1/\lambda + \frac{a/c}{\alpha' + n\beta'} = 1/\lambda\infty. \qquad (2)$$

This equation contains four constants, α', β', a/c and $\lambda\infty$. But a/c and $\lambda\infty$ are dependent on e, so that the constants, given e, are α', β' and $\lambda\infty$. Two of these, α' and β', may be fixed by the condition that the equation shall be satisfied for two pairs of λ and n, i.e., that its graph shall pass through two of the plotted points derived above by measurement of the trail. $\lambda\infty$ is then found by trial and error, by assuming an elongation e of A from the radiant (or, vice versa, of the raidant from A), and plotting enough points on the graph of (2) to see whether the graph fairly repre-

sents the plotted observations. This graph may be called a perspective curve, as it represents a distribution of points along CD such as points uniformly distributed along AB would give by perspective alone.

After three trials it was found that, for AM 1582, with $e = 90.0°$, the perspective curve cut the row of points in seven points; for AM 6090, with $e = 25.6°$, the row was cut in four points. These results were regarded as sufficiently good approximations.

Now the radiant must lie in the path prolonged backward on the sky, and must be 90° from the pole of the trail. The pole of each trail having been taken as the pole of a great circle through two extreme points determined by star-chords and the point C on each trail being known, the celestial position of each radiant could be found. The results were:

AM 1582, radiant near 22^h41^m $+12°36'$.

AM 6090, radiant near $4^h49.3^m$ $-45°33'$.

In figures 2 and 3 the final perspective lines are plotted on the series of observational points. It will be noted that the distribution of observational points agrees very well with a perspective distribution, provided the flicker on the path was periodic.

Periodic flickering might be due to non-homogeneous composition of the meteor, combined with rotation; so that now a more refractory surface, now a less refractory, is exposed to the hot blasts in front, with correspondingly varying rates of evaporation and hence of brilliancy; one flash for each rotation, it may be. On this hypothesis the near agreement of each row of observational points with its perspective line is explained by a very nearly constant linear velocity of the meteor, combined with a slightly varying angular velocity. Then, too, the areas of low boiling point would be altered by ablation, and errors of measurement must be admitted; but these last can hardly bear the whole responsibility.

In figure 1 it will be seen that toward the brighter end of the trail the previously quite uniform distribution of spindles is succeeded by a smear of light, in which counting was impossible, and this is followed by a new distribution of spindles, in which the intervals are much shorter. On measuring, it was found that the successive differences were such as to indicate that the period of the old single series was still retained, but that there were two series superposed, out of step. On plotting, these two series were separated, and are shown by the double row of points at right of figure 3. These two rows were brought up to the perspective curve at their left-hand ends, for the count in the smear was completely lost, and the abscissas had to be treated somewhat arbitrarily. The slope of one row is nearly that of the perspective line, while the other slopes off to the right and lower. We may suppose that the original single object broke into two pieces and dust. The greater area exposed caused increased evaporation and greater brilliancy, with all the effects of rotation

submerged in the cloud; hence the smear. The dust having been quickly destroyed, the larger fragments travelled on with slightly different velocities; hence the non-parallelism of the plotted rows thereafter. But one must admit the objection that the pieces are unlikely to retain the original rate of rotation little changed. And to the whole rotation hypothesis there is an objection, that the beginning of a trail is always a hair-line with no spindles for some distance. More information is needed.

The plotted series in case of *A M* 1582 is rather short, because of faintness of spindles, and the difficulty of counting after a certain point.

THE UNI-MOLECULAR DECOMPOSITION OF AZO-METHANE; THE ADEQUACY OF ACTIVATION BY COLLISION

By Bernard Lewis[1]

School of Chemistry, University of Minnesota

Communicated May 23, 1927

Introduction.—The purpose of this paper is to apply the recent admirable attempt by Fowler and Rideal[2] to account for the rate of uni-molecular reactions on the basis of activation by collision, to available data on a new uni-molecular reaction. The work of Ramsperger[3] on the decomposition of azo-methane ($CH_3N:NCH_3$) shows quite well that it takes place in a homogeneous, uni-molecular manner. It will be shown that with a very conservative estimate of the number of effective internal degrees of freedom, the rate of decomposition of azo-methane can be adequately accounted for on the basis of activation by collision. The lack of specific heat data on this and other complex molecules which decompose uni-molecularly is a hindrance to an exact evaluation of the degrees of freedom which are totally or partially activated and it is hoped that the recent concentration on the kinetic problem of uni-molecular reactions, in general, may stimulate, as well, the coöperation of specific heat investigators in this direction.

It appears to the writer, and it has been expressed previously, that it is not a mere accident that all substances discovered so far which decompose in a uni-molecular fashion are rather complex molecules able to store large amounts of energy which must show up in abnormally large heat capacities. Nor is it a mere coincidence that the heats of activation, as calculated from data on temperature coefficients with the aid of the Arrhenius equation, are also large indicating the necessity for active molecules with relatively large amounts of energy above the average. That complex molecules have large specific heats may be gathered from the

recent determination of the molal heat capacity of N_2O_4 by McCollum.[4] He finds that the molecular heat increases from 11.4 calories per degree at 33.7°C. to 19.5 at 160°C. N_2O_4 being rather unstable it is to be expected that many of the vibrational degrees of freedom are effective. Assuming a symmetrical structure with one of the nitrogen atoms as a rigid framework, one can account for a molecular heat capacity of 15 calories per degree on the basis of effective degrees of freedom (3 translational; 3 rotational; at least 6 vibrational, kinetic and potential (at the higher temperatures), for the O atoms; and 3 vibrational, kinetic and potential, of one N O_2 with respect to the other). This is far from the maximum number possible.

Application to Azo-Methane.—The expression[5] developed by Fowler and Rideal for the number of collisions with available energy for redistribution greater than ϵ_0 is

$$\frac{2(2\pi)^{1/2}N_1N_2\sigma^2}{\Gamma(1/2S_1+1/2S_2+2)}\left[\frac{m_1+m_2}{m_1m_2}kT\right]^{1/2}\left(\frac{\epsilon_0}{kT}\right)^{1/2s_1+1/2s_2+1}e^{-\frac{\epsilon_0}{kT}} \quad (1)$$

where N_1 and N_2 are the number of molecules per cc.; σ, the sum of the radii of the colliding molecules, in this case the diameter of one molecule; m_1 and m_2 the masses of the participating molecules; s_1 and s_2 are the variable (coördinates or momenta) comprising the Hamiltonian energy function ϵ which contribute classical square terms to the internal energy of the molecule. It has been shown by Fowler and Rideal that $s = 2r$ where r is the number of internal degrees of freedom possessing both kinetic and potential energy. Degrees of freedom possessing only kinetic energy such as rotational have only one square term in the energy function.

It is implicitly assumed that a collision between two molecules, the sum of whose energies above the general average is equal to the heat of activation will result in the activation of one of them which may or may not decompose. The difficulty which Tolman, Yost and Dickinson[6] experience intuitively is not shared by the writer. It seems perfectly natural for an active molecule to wish to revert to its normal state a phenomenon with which we are not unfamiliar as in the spontaneous emission of radiation by excited molecules or in certain collisions of the second kind. To accomplish this as far as is possible all this extra energy might easily flow into one of the colliding molecules resulting finally in its disruption. It is quite conceivable that some internal perturbation may facilitate at some moment the reception of energy and at another moment the emission of energy provided the conditions obtain which provide the giver or acceptor of energy. This conception need involve nothing more than a natural continuous change in internal phases and it is even possible for no energy interchange to take place under the proper internal conditions. The writer is cognizant of the difficulties to be overcome and with our

very small knowledge of these processes of energy transfer one cannot be too rigorous in his assertions.

At the experimental temperature of 600°K. one expects the groups in $CH_3N:NCH_3$ to have fully excited classical vibrational energies. In particular, this will be true of the CH_3 groups since they seem to be highly oscillating, the experimental result being their severance from the rest of the molecule. The hydrogens certainly should possess half their classical oscillational energies. We shall, however, assume only those degrees of freedom which the mode of decomposition tells us must be fully excited. Assuming in the extreme the rigidity of both nitrogen molecules, there are 3 degrees of freedom with respect to vibration for each CH_3 yielding 6 square terms for each. The rotational energies are fully excited at this temperature and represent 3 freedom or 3 square terms (the molecule does not lie on a straight line). Since the derivation admits only those variables contributing square terms to the internal energy of the molecule, degrees of freedom with respect to translation cannot be included. The number of possible freedoms which are active is much larger but only 15 square terms will be assumed.

To be still more on the safe side s will be taken to be

$$s_1 = s_2 = 14 \tag{2}$$

in the following calculations. It is necessary to distinguish between the heat of activation Q, an observed quantity calculated from the Arrhenius equation,

$$\frac{d \log K}{dT} = \frac{q}{kT^2} \tag{3}$$

and ϵ_0 the theoretical energy of activation employed by Fowler and Rideal. Since $\frac{\epsilon_0}{kT}$ is large, their relation (25) will be used

$$\epsilon_0 = q + (\tfrac{1}{2}s - 1)kT. \tag{4}$$

Ramsperger's data for experiment 20 will be employed, although any experiment would do equally as well. From the temperature coefficient $Q = 51{,}200$ calories. At 571°K.,

$$\frac{Q}{RT} = \frac{q}{kT} = 45.1$$

$$\frac{\epsilon_0}{kT} = \frac{q}{kT} + (\tfrac{1}{2}s - 1) = 45.1 + 6 = 51.1.$$

If the two colliding molecules are of the same kind every collision is counted twice over in (1) since it is derived as collisions between molecules A with

ϵ_1 and B with ϵ_2 and also A with ϵ_2 and B with ϵ_1. The factor two must be removed. Using $\sigma = 10^{-7}$ cm. (this is within reason for such a large molecule) and $N = 6.83 \times 10^{18}$ molecules/cc. from the mean experimental pressure for the first 10 minutes, and substituting in equation (1) one gets

$$\frac{(2\pi)^{1/2}(6.83 \times 10^{18})^2(10^{-14})}{15!}\left(\frac{2 \times 8.3 \times 10^7 \times 571}{58}\right)^{1/2}(51.1)^{15}e^{-51.1}$$

or the rate of activation is 1.07×10^{20} molecules per cc. per second. Comparing this with the observed rate of decomposition which is 1.67×10^{15} molecules per cc. per second one finds that the maximum rate of activation is about 100,000 times larger than the observed rate of decomposition.

It is clear, that with what the writer believes to be a very conservative estimate of the complexity of the molecule azo-methane, here is another case of a uni-molecular reaction where activation by collision proves adequate to sustain an ample supply of active molecules.

[1] NATIONAL RESEARCH FELLOW.

[2] *Proc. Roy. Soc.*, **113**, 571, 1927.

[3] *J. Amer. Chem. Soc.*, **49**, 912, 1927.

[4] *Ibid.*, **49**, 28, 1927.

[5] This expression first appeared in a paper by B. Lewis and E. K. Rideal, *J. Amer. Chem. Soc.*, **48**, 2553, 1926.

[6] *Proc. Nat. Acad. Sci.*, **13**, 188, 1927.

ON X-RAY DIFFRACTION PATTERNS FROM LIQUIDS AND COLLOIDAL GELS

BY G. L. CLARK, R. H. ABORN, E. W. BRUGMANN AND R. L. DAVIDSON

DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Great interest is being displayed now in the interpretation of the X-ray diffraction patterns which are obtained from non-crystalline substances. When monochromatic X-rays, defined by pinholes, pass through liquids, gels, glasses, etc., the diffracion pattern is registered as one or more broad rings or haloes on the photographic film. There has been considerable controversy over the significance of these "amorphous" rings, but Zernicke and Prins[1] have recently deduced mathematically, with great success, that the broad rings are indicative of the natural distance of nearest approach of molecules in disordered thermal agitation, rather than of regularity of arrangement of atoms in molecules, chance lattice formation, crystal fragments, etc. Excellent new experi-

mental evidence has been obtained by Stewart and Morrow[2] on primary normal alcohols, which show two spacings for the liquids, one corresponding to the length and the other to the cross section (essentially constant) of the molecules, in every way analogous to the results with crystals. Raman and Sogan[3] have sought to obtain information concerning geometrical forms of molecules from the sharpness of the rings as a measure of homogeneity in X-ray scattering by comparison of the patterns of cyclohexane (sharp) and hexane (diffuse).

Most of the calculations of spacings have heretofore been made upon the basis of the Ehrenfest formula $a = \frac{7.72\,\lambda}{4\pi \sin \theta}$, $2\,\theta$ being the angle of the diffracted cone of rays. This formula was derived for the condition of regularity of spacings of atoms in molecules and has given results agreeing with spacings calculated from molecular weights and densities, assuming spheres, even for monoatomic liquid argon. However, recent developments should give weight to the classical Bragg equation $n\lambda = 2d \sin \theta$, which gives results about 0.81 as great as the Ehrenfest formula.

New practical significance in these "amorphous" patterns has been sought in the attempt to discover, for example, the structure of unstretched rubber. The fact that stretched rubber yields sharp, crystal-like, fiber patterns requires explanation in terms of original structure. Hauser and Rosbaud[4] have measured the spacings of the haloes for ordinary latex films as 14.88 A.U. (inner ring) and 6.05 A.U. (outer ring). They find also that metastyrol gives the same spacings. This is verified by Hünemörder[5] who shows also that for liquid styrol the outer ring appears in the same position but the inner ring observed in polymerized metastyrol is missing. Katz[6] has measured the haloes for the following pairs of substances, unpolymerized and polymerized: isoprene and rubber, styrol and metastyrol, dicyclopentadiene and cyclopentadiene-rubber, acrylic acid and polymerized acid, liquid and polymerized china wood oil. Upon the basis of eye measurement of diffraction ring diameters he comes to the conclusion that there is no change in spacings upon polymerization.

It seems of interest to present a few of the observations on X-ray patterns for amorphous substances made in the writers' laboratory. These tend to show that very important information of practical bearing can be obtained on rubber and its substitutes, nitrocellulose, gelatine, linseed oil, china wood oil, resins, varnishes, etc. In all cases the films have been photometered so that on the curves the exact centers of the broad bands are easily located. For unstretched rubber latex films the spacings calculated by the Ehrenfest formula from the two principal rings (second order faint rings appear in addition) are 6.03 and 14.76 A.U., in fair agreement with Hauser and Rosbaud. When, however, the rubber is very carefully purified by a process of fractional solution and evacuation

to constant weight, the spacings are 5.97 and 11.15 A.U., a profound change in the inner ring. Intermediate values up to 14.76 A.U. have been observed with solvent swelling.

With nitrocellulose of the same composition the following quantitative results are typical for the spacings of the inner and outer rings, respectively, calculated by the Bragg formula:

	FRESH	AGED (LIGHT)	AGED (HEAT)
Untreated, dry	7.18 A.U. 4.02	7.17 A.U. 4.05	6.98 A.U. 3.92
Dry, residual solvent present	9.30 4.47	9.32 4.47	7.86 4.31
Oil softener added	7.34 4.31	... 4.39	... 4.39

The swelling or combination of molecules with solvent or oil has a much greater effect on the X-ray pattern than aging, even though the nitrocellulose film may become very brittle.

Contrary to the results of Katz, distinct though usually small differences in spacings are observed with china wood oil and linseed oil during polymerization and drying. The following remarkable results on china wood oil were obtained by careful measurement of the photometric curves; they are expressed as percentage change related to the spacings of the raw liquid oil calculated by the Bragg formula:

	INNER RING	OUTER RING
Raw liquid	8.5 A.U.	4.4 A.U.
Raw dry film (oxidation at room temperature)	+6%	+1%
Raw gel (polymerized by heat)	+3%	+2%
Prepared liquid	+12%	+16%
Prepared dry film	+13%	+ 6%

The prepared liquid in this case consisted of china wood oil heated with Venice turpentine and thinned with pure turpentine. The film dries with a crystalline finish which is, however, only a pseudo-crystalline, wrinkled skin. The increase in spacings (decrease in ring diameters) in every case including drying over those of the raw oil is remarkable. Combination with solvent molecules and polymerization are both definitely indicated. No indication has been found in these patterns of long spacings such as are obtained with solid carbon-chain compounds. It is possible that diffraction rings corresponding to these long spacings may be so close to the central direct-beam trace on the photographic films that they are not defined. This is particularly true where Mo-Kα rays have been used instead of rays from a copper target.

Similar results have been obtained with cumar, resins, varnishes, etc. In all cases it is clear that the "amorphous" ring diagrams may yield very important theoretical and practical results in terms of fundamental space

array of molecules or aggregates acting as units, polymerization, the swelling of gels and changes during aging. X-ray science has reached the stage wherein it may analyze all matter in any form whatsoever.

[1] *Zeit. Physik*, **41**, 184 (1927).
[2] These PROCEEDINGS, **13**, 222 (1927).
[3] *Nature*, **119**, 601 (1927).
[4] *Kautschuk*, Jan., 1927, p. 17.
[5] *Ibid.*, Mar., 1927, p. 106.
[6] *Zeit. physik. Chem.*, **125**, 321 (1927).

THE EFFECT OF TUBERCLE BACILLI AND THE CHEMICAL FRACTIONS OBTAINED FROM ANALYSIS ON THE CELLS OF THE CONNECTIVE TISSUES IN RABBITS

BY FLORENCE R. SABIN AND CHARLES A. DOAN

THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH, NEW YORK CITY

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Under the auspices of the Research Committee of the National Tuberculosis Association, we have been making some of the biological tests of the proteid and phosphatid fractions which have been isolated from human tubercle bacilli. Two specimens of water-soluble proteids, 304 and 903, were received from Prof. Treat B. Johnson of Yale University and two phosphatid fractions, A-3 and A-4, from Dr. R. J. Anderson of the same laboratory. The effects of these chemical fractions are to be expressed in terms of the same phagocytic mononuclear cells as are involved in the infection itself.

In the study of infections, in general, increasing emphasis is being laid on the part played by the phagocytic mononuclear cells of the connective tissues. All the investigators who are employing the method of tissue culture find evidence of the transformation of fibroblasts and monocytes into macrophages, and the reverse, and hence tend toward the view that these mononuclear cells are of one strain and that any differences in their morphology and activity are due to environment.

In our work, with living tissues taken directly from the animal for supravital studies, we have found differences in the reaction of clasmatocytes and monocytes to tubercle bacilli, which seem to indicate a distinction of cellular response. In supravital studies, neutral red affords the advantage of a chemical indicator; its range in pH is from 6.8 to 8; toward the acid side it is a brilliant scarlet; its alkaline reaction is yellow. The optimum dilution of the dye, when it is to be used as a physiological indicator, is tested in normal blood by the scarlet reaction of the granules

of the basophilic leucocyte at one extreme and the yellow color of the granules of the eosinophile at the other. In such dilution, the vacuoles of the monocyte are a salmon red, probably close to the neutral reaction; in becoming the epithelioid cell of the tubercular infection, the reaction of the vacuoles tends toward a clear carmine tone. With the clasmatocyte or macrophage on the other hand, with its marked power of phagocytosis, there is a wider range of color in the vacuoles of digestion. Much debris, especially dead leucocytes within the clasmatocyte, stains red, but there is a strong tendency for the vacuoles to become yellow rapidly while the cell is watched at 37°C. Many of the clasmatocytes directly from the animal show the yellow or alkaline reaction of the dye.

In supravital studies on tubercular rabbits, starting twenty-four hours after inoculation and carried out in the series through the acute and the chronic reaction to the disease, it has been found that clasmatocytes fragment the bacilli easily and readily as shown by the acid-fast debris of them within the cells; while the epithelioid cells and the giant cells derived from the monocytes retain large numbers of intact bacilli.

The proteid fractions were given to seven rabbits, in doses of from 1 to 20 cc. of a saturated aqueous solution intravenously. One animal died acutely immediately after the first dose of 903 and another immediately after the second dose. The experiments have shown that 903 is the more potent, more toxic form. The general effects were the same on the remaining five animals. The peripheral blood was followed almost daily. All the animals showed an anemia and a rhythmic rise in monocytes. These monocytes were somewhat stimulated but no epithelioid cells were found in the blood. At autopsy all the animals showed an increase in clasmatocytes in the tissues, especially in the lungs. The interalveolar septa were thickened so that some of them were wider than the diameter of the air sacs themselves. There were hemorrhages, most marked in the retroperitoneal tissues, in the psoas muscles and in the bone marrow. The proteid fractions were toxic; all the animals had fever between 107° and 108.5°.

The phosphatid fractions were given intraperitoneally in the form of an emulsion. The effect was the same in the four animals used; the material was entirely non-toxic but there was an extensive local development of epithelioid cells and giant cells making typical tubercular tissue. The omentum was greatly thickened and nodular; the mesentery, the peritoneal surface of the intestines, the surface of the pelvic organs and the parietal peritoneum were extensively involved.

There were some intact tubercle bacilli in the original phosphatid fractions; both these bacilli and the fat itself reacted to the carbol-fuchsin. However, these bacilli were dead; they were of the human strain H 37; ten guinea pigs were inoculated with the fractions directly or after passage

through the rabbits and all have been negative to repeated tuberculin tests. Five of the guinea pigs were non-tubercular as proved at autopsy and five are still alive, in good condition four months after inoculation. No bacilli were found in the lesions in any of the rabbits receiving the phosphatid fractions, possibly because they had been fragmented by clasmatocytes. It was already known that dead tubercle bacilli give rise to tubercular tissue. In these experiments, however, the extent of the tubercular tissue has been far greater than could have been produced alone by the small numbers of dead bacilli incidentally introduced with the fat. This has been demonstrated by control experiments with repeated doses of comparable amounts of dead bacilli which gave only a limited reaction of tubercular tissue.

These studies show that the proteid fractions are toxic, are associated with a damage to endothelium producing hemmorhage and give a pressor effect on clasmatocytes, while the phosphatid fractions give a local production of typical tubercular tissue.

THE EMBRYOLOGY OF EQUISETUM DEBILE ROXB.

BY D. H. CAMPBELL

DEPARTMENT OF BOTANY, LELAND STANFORD UNIVERSITY

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The genus Equisetum includes about twenty-five species, the sole survivors of a very ancient group of plants. A knowledge of the embryo is, therefore, of great importance in determining their relationships to the other Pteriodophytes.

No comprehensive study of the embryo has been made since that of Sadebeck in 1878, although several contributions to the subject have been made since.

A large number of gametophytes of *E. debile* was sent the writer from India. These contained great numbers of embryos in all stages of development, so that it was possible to secure an almost complete series showing the early history of the sporophyte.

E. debile differs considerably in some of the details of the embryo from the species (*E. arvense*, *E. palustre*) studied by Sadebeck, and more nearly approaches *E. hiemale* and *E. variegatum*.

The most important point brought out in these investigations is the origin of the buds from which the secondary shoots develop. These buds are of endogenous origin, and sometimes, at least, arise from the root, thus closely resembling a primitive Fern, Ophioglossum. This fact supports the view already expressed by the writer, that there is a real, if some-

what remote relationship between the Equisetineae and the most primitive Ferns.

Both from its size and from the many sporophytes produced from it, the gametophyte of *Equisetum debile* is strongly reminiscent of certain liverworts, especially Anthoceros.

THE EFFECT OF SMALL AMOUNTS OF CHEMICALS IN INCREASING THE LIFE ACTIVITIES OF PLANTS

BY F. E. DENNY

BOYCE THOMPSON INSTITUTE FOR PLANT RESEARCH

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Many chemicals in numerous ways increase the rate of growth of plants. But I desire to exclude from this discussion those that are ordinarily regarded as fertilizing elements or those which furnish building material, or yield energy to the plants by oxidation. The substances to which reference is made are those that act in a manner not now well understood, which are not regarded as being utilized directly as food and which produce results seemingly out of proportion to the energy they could furnish even if they were absorbed and oxidized. I must further restrict the discussion mainly to those chemicals with which I have had experimental experience.

The influence of small amounts of chemicals in increasing the life activities of plants may be illustrated by the experiments on the coloration of citrus fruits by the use of ethylene. Lemons and oranges may be commercially mature and yet have considerable amounts of green color in the rind. If such fruits after being harvested are stored under favorable conditions, the green color will disappear and will be replaced by the desired yellow or golden color.

It had been known for a long time that heating the storage rooms with kerosene stoves reduced the time required for coloration to about one-fourth the usual time. It was thought that this increased rate of coloring was due to the conditions of temperature and humidity within the heated rooms, but Sievers and True[1] showed that the results were produced mainly by the gaseous combustion products from the kerosene stoves. My experiments,[2,3,4] in 1922 and 1923 indicated that the effective gas in causing these changes was ethylene (C_2H_4).

Hence it was found possible to dispense with the kerosene stoves and to substitute for them the pure gas itself. Since ethylene was obtainable as a compressed gas in cylinders at a reasonable price its use was found to be commercially possible. The new method has been quite

generally adopted in practical work in California and to a certain extent in Florida.

Surprisingly low concentrations of ethylene added to the air surrounding the fruit are able to bring about hastened coloration. If precautions are taken to prevent the loss of ethylene by diffusion, the process is successful with 1 part ethylene to 10,000 parts of air, 1 part in 100,000 or even 1 part in 1,000,000. In practical operation a somewhat higher original concentration is used in order to take care of losses of gas, but it has not been necessary to use a greater concentration than about 1 cubic foot of ethylene to about 5000 cubic feet of air.

A study of the respiration of lemons exposed to these low concentrations of ethylene showed that the life processes of the fruit were greatly increased.[5] The rate of production of carbon dioxide was doubled or even trebled in 48 hours by exposure to air containing ethylene in concentrations of 1 part in 1000, 1 part in 10,000 or less. These experiments were interesting in showing that after the respiration of a given lot of fruit had been increased by the use of ethylene, a discontinuance of the exposure to ethylene led to a fall in the previously high rate. The rate did not fall to the original value before the ethylene was applied, but the results indicate that the effect of the ethylene was not to start a series of reactions that could proceed in its absence, but suggested that the continued presence of ethylene was necessary to maintain this high respiration rate.

The mechanism of this great increase in respiration is not known at present. We should consider first whether treatment with ethylene makes available in the tissue additional amounts of oxidizable substances. E. M. Harvey[6] who made the first measurements of the effect of ethylene upon the metabolism of the plant showed in 1915 that as a result of exposure of sweet-pea seedlings to ethylene the proportion of the simpler forms of sugars, and of amino acids and amides, was increased. These results were confirmed in certain respects by the later work of Rosa[14] with tomatoes, and more recently by that of Regeimbal and R. B. Harvey.[7] But in the experiments of E. M. Harvey this increase in these forms of chemicals did not, in general, lead to an increase in respiration; decreases were observed in all cases except at the shortest period of exposure. It appears, therefore, that other factors in addition to the amount of oxidizable materials are involved.

It has been proposed that the rate of production of carbon dioxide in respiration is related: to oxidizing enzymes such as oxidase, peroxidase and catalase;[8] to reducing enzymes such as dehydrase, Wieland;[9] to the activity of the dipeptide, glutathione, Hopkins;[10] to the presence of pigments such as cytochrome, Keilin;[11] to the catalytic activity of iron, Warburg.[12] But we do not yet know how such small concentrations of ethylene can so modify the behavior of these substances as to cause such a large

increase in the rate of respiration. It may be necessary to consider that the primary effect of the ethylene is upon the protoplasm itself, and that the coöperation of these factors in increasing the output of carbon dioxide is secondary.

A further possibility in this connection may be related to the discovery of the anti-oxidizing substances by Moreau and Dufraisse,[13] who found chemicals that were able to retard oxidation; if there are oxidation retarders in plant tissue it is possible that ethylene may modify the action of such rate-controlling substances either directly or through its effect on the living substance.

Returning now to the experiments on the coloring of citrus fruits, it was found that high concentrations of ethylene, too high temperatures, too low temperatures and lack of oxygen prevented or retarded coloring. That is, conditions favorable for the life processes of the fruit were also favorable for coloring. These facts and those obtained in measuring the increased respiration of the treated fruits indicated that the effect of the ethylene was to hasten the processes that normally occur in the fruit after detachment from the tree, so as to bring about in a short time changes which, in the absence of ethylene, required a longer time for completion. They show that the ethylene is acting in a physiological and not in a directly chemical manner, that by some method not now understood the general level of life activity within the tissues of the plant is raised.

Subsequent experiments by others have shown that these stimulative effects of ethylene are not restricted to citrus fruits. Thus Rosa[14] showed that the coloration of tomatoes was hastened by ethylene; during this process the acidity of the fruits was decreased and the proportion of soluble nitrogenous compounds was increased. Rosa[15] also found that the rest period of dormant buds in the potato could be shortened by suitable treatment with ethylene. Using methods similar to those developed in California for citrus fruits, R. B. Harvey[16] reported favorable results in the blanching of celery. Wallace[17] was able to force the development of dormant buds on apples and other species; he also noted the renewed growth of lenticle tissue with the formation of excresences.

There is evidence in the older experiments, in which the toxicity of ethylene for plants was mainly investigated, that the life activities at least of certain tissues or groups of cells were increased by ethylene; thus the swelling of stems, observed by Knight and Crocker,[18] the enlargement of cells and increased cell divisions in roots, noted by E. M. Harvey and Rose,[19] the prolifications of tissue in lenticles and leaf-scars described by Doubt,[20] can be regarded as being the results of a renewal of growth or increased life processes of the cells in these regions of the plant body.

Further illustrations of stimulative chemical effects are found in the results of treatments designed to break the rest period of Irish potatoes.

Freshly harvested tubers, if replanted under conditions favorable for growth, do not sprout at once but require a period of after-ripening. The depth of dormancy varies with the variety but is generally two months or more.

The experiments of McCallum[21] in 1909 showed that exposure of the potatoes to the vapors of such chemicals as ethyl bromide, ethylene dichloride, carbon tetrachloride, ammonia, bromine and gasoline would induce early sprouting. Rosa[22] in 1923 obtained sprout-forcing effects with solutions of sodium nitrate.

I extended these results[23,24] by testing the effects of a large number of chemicals (at this time about 240) at different concentrations and with various periods of treatment. McCallum's results with the first three chemicals in the list above, and Rosa's with sodium nitrate were corroborated and in addition the following chemicals were found to induce sprouting in advance of untreated tubers: ethylene chlorhydrin, the thiocyanates of sodium, potassium or ammonium, thiourea, carbon bisulphide, trichlorethylene, dichlorethylene, ethyl iodide and xylol.

With the Bliss Triumph variety especially favorable results were obtained with ethylene chlorhydrin ($ClCH_2CH_2OH$). A suitable method consists in dipping the tubers (cut into pieces ready for planting) into a solution consisting of about 30 to 40 cc. of 40% ethylene chlorhydrin per liter of water, removing the dipped potatoes and storing them 24 to 48 hours in a closed container. The vapors of the chlorhydrin come in contact with the dormant potato buds and in some manner induce prompt sprouting. The gain in time of sprouting depends on the stage of dormancy of the potato at the time of treatment but varies usually from 2 to 6 weeks.

Other varieties such as Irish Cobbler and Green Mountain responded in a somewhat better manner to treatment with thiocyanate solutions. Soaking the cut tubers for 1 hour in a 1 to 2% solution of thiocyanate (sodium, potassium or ammonium) broke the rest period and caused prompt sprouting.

Further experiments showed that the dormancy of the buds of woody twigs of apple, grape, plum, lilac and locust could be forced into growth in the autumn and early winter by exposure to low concentrations of ethylene chlorhydrin, acetaldehyde and ethylene dichloride. The gain in time of budding of grape and apple cuttings was about 2 months. Experiments have been undertaken to determine whether these results can be applied in a commercial manner for forcing early blooming of certain potted plants which are favorites in the florist's trade but which have a long dormant period and are slow in coming into bloom.

An interesting point in connection with these experiments is that so many different kinds of chemicals were able to induce sprout or bud development. An examination of the list of chemicals shows no evident relation between the effectiveness of a chemical and its molecular grouping.

When we come to consider the question how these chemicals can cause this increase in activity and renewal of growth, we find that the first difficulty relates to our lack of knowledge of the causes of dormancy or retardation in growth. Johannsen,[25] the pioneer worker in this field, shows that lack of growth in these organs cannot be due to a deficiency in the ordinary nutrients such as sugar. In fact, Hooker[26] has suggested that repression of growth is correlated not with a deficiency but with an accumulation of carbohydrate.

If food supply were the principal factor we should expect that a gradual change in stored food would take place during natural after-ripening. The experiments of Appleman,[27] however, showed, at least for potato, that no significant change in the starch, sugar or nitrogenous compounds took place during the period preceding the renewal of growth. There is little evidence in my experiments that the chemicals used were acting in a nutritive way. The fact that so many different chemicals were able to produce the same or a similar result shows that the action here must be indirect, that the chemicals used did not furnish food or energy, but caused some internal physiological condition which, in a manner not now understood, led to a renewal of growth.

An important factor in these results as well as in many of the results obtained by previous workers is that forcing appears to be related to incipient injury. If the concentration of chemical is great enough the tissue is injured or killed. But at concentrations of chemical and periods of exposure just below the point of injury, stimulation of the tissue into renewed activity occurs. It may be that this slight injury to the tissue changes the semi-permeable character of the plant membranes (as suggested by Coville,[28] in the case of plants subjected to low temperatures), weakening the membranes, and allowing greater rates of diffusion of enzymes, or food material. An increased permeability to oxygen may also be important since, according to Appleman,[27] oxygen supply to the tissue was found to be a critical factor in his experiments with potato.

Suggestive evidence on this point has also been provided by Carrel and Baker[29] who found that the substance in embryonic tissue which markedly stimulated the multiplication of isolated cells was a product of the partial hydrolysis of a protein. Neither the protein itself nor the products of its complete hydrolysis were effective, but when the hydrolysis of the protein was continued for about 3.5 hours the resulting liquid containing proteoses and other products of partial hydrolysis caused rapid multiplication of the cells. These results may throw some light on the experiments in forcing the buds of potatoes and other plants. It is possible that the slight injury that is produced causes a partial decomposition of constituents of the tissue resulting in the releasal of growth-promoting substances which start up renewed cell division and bud growth.

The enzyme activity of the treated plants should be studied especially with the view of determining the effect of the treatment upon the hydrolytic processes occurring in the tissues. The types of reaction that are favored by the treatment, the nature of the substances formed and their effect upon growth should give valuable information regarding the mechanism of the response.

In conclusion: I have described a number of experiments in which favorable results have been obtained in increasing the life activities of plants by chemical treatments. The chemicals that were found to cause this stimulation varied greatly in chemical character, so that no evident relation could be found between the type of chemical used and the result obtained. In most cases it did not seem possible that the substance was used by the plant directly as food, and in no case could it have supplied sufficient energy to account for the resulting increased activity. The mode of action of these chemicals, the details of the methods by which plant processes, previously inhibited or retarded, are induced to start again at a quickened rate are not now understood. I discussed the results from the viewpoint of certain theories regarding life activities in plants but it must be understood that the suggestions made do little more than indicate the sort of experimental work that may be needed to test the hypotheses that have been proposed.

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[24] *Ibid.*, **13**, 1926 (386).

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THE ARCHITECTURAL EVOLUTION OF PUEBLO BONITO

BY NEIL M. JUDD

U. S. NATIONAL MUSEUM, WASHINGTON, D. C.

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Pueblo Bonito is a prehistoric Indian village in northwestern New Mexico. Since 1921 annual explorations have been pursued there by the National Geographic Society. As a result the village has been entirely laid bare and much of its ancient history recovered. From this archeological record, we judge Pueblo Bonito to have been abandoned approximately one thousand years ago. The Bonitians had no beasts of burden; no metal tools.

On the present occasion we are to concern ourselves solely with the architectural development of Pueblo Bonito and shall have nothing to say regarding those remarkable cultural achievements that made it the most influential settlement in the southwestern United States in pre-Columbian times.

Pueblo Bonito covers over three acres of ground; it is semi-circular in plan, its straight south side being 518 feet long. There are nearly three hundred rooms on its ground floor; portions of four story walls still stand. In its heyday, Pueblo Bonito included approximately eight hundred rooms and sheltered between twelve and fifteen hundred individuals. These were farmers; they cultivated maize, beans and squash in neighboring fields.

The population of Pueblo Bonito included two distinct peoples. These were entirely unlike despite the basic similarity of their respective cultures. Their architecture was different; the product of their minor industries differed. They doubtless spoke different languages. But they dwelled together here, in apparent harmony, for a long period of time.

The first group, the actual founders of Pueblo Bonito, lived there several generations before the second group came in to dominate the settlement and create for it a prestige, the influence of which was felt as far away as the Pacific Coast and even the valleys of central Mexico. The first group produced a single type of masonry; the second, being more progressive, created three types.

In brief, these four methods of construction may be described as follows: The first type consists of rather large sandstone slabs, chipped on the edges and laid in an abundance of adobe mud; the second type, that is, the first utilized by the new-comers to Pueblo Bonito, is characterized by sizable blocks of soft, friable sandstone, pecked or rubbed smooth on the face only and chinked with innumerable small, thin chips of laminate sandstone; in the third type, blocks of laminate sandstone, approximating one inch in thickness, are laid to form courses which tend naturally to relegate the dressed blocks of friable sandstone into bands, a foot or more apart; in the fourth method of construction the dressed blocks were entirely eliminated, the dark, laminate sandstone being exclusively employed.

The old, original village contained no external first-story doors. Lower rooms were entered through hatchways by means of ladders to the roof tops; within, they connected one with the other. These first type dwellings varied in size and ceiling height; their walls were habitually unsystematic and of unequal thickness. Additions to this portion of Pueblo Bonito were made haphazard with the result that the original outside wall was markedly irregular.

When the second group of people came to dwell in Pueblo Bonito, their first houses formed a single tier inclosing the older settlement and correcting the irregularity of its outer wall. These newer rooms were surprisingly uniform in shape and size; carefully smoothed willows rested on poles to form their ceilings. Outside doorways appeared in the first-story rooms but these doors were later blocked and plastered over.

With the introduction of the third masonry type, Pueblo Bonito witnessed a period of reconstructional activity. Most of the second type rooms were razed and over-built; the plaza, for celebration of public ceremonials, was enlarged and divided. All the extra-mural developments associated with Pueblo Bonito belong to this epoch. It seems reasonable to suppose that the Bonitians at this time were experiencing their maximum power and influence. Indian traders on foot came with live birds from the highlands of Mexico and with shells from the Pacific Coast to exchange for the turquoise of Pueblo Bonito. And all the while the old, conservative group continued to live in its corner of the great communal settlement almost wholly uninfluenced by the arts and industries of their immediate neighbors.

The fourth, or final type of construction, is restricted largely to the southeastern quarter of the village. It is the best preserved of the four types and has best withstood the passing centuries. But this last addition represents a compromise between dominating personalities in the village. Plans for a considerable addition to Pueblo Bonito were well under way when those plans were abandoned and this fourth section substituted. Foundations for this contemplated addition had been completed; they

extended five hundred feet beyond the easternmost wall of the pueblo proper. Within the latter, the fourth type walls rest immediately upon this abandoned foundation series.

Throughout all except that portion of Pueblo Bonito occupied by the first group, evidence is found of successive alterations. Walls were torn down and rebuilt a few feet away; dwellings gave way to circular, ceremonial chambers. The foundation stones of razed walls were usually left undisturbed; they measure the degree of reconstruction that occurred within the walls of Pueblo Bonito during its long-continued occupancy. They give evidence also of the modest value the Bonitians put on their own labor.

External doors in rooms of second type construction were later blocked. and plastered over. In rooms of third and fourth type masonry, no outside doors occurred; small ventilators in the upper walls were reduced in size or completely blocked. These facts, taken with other evidence, disclosed during the course of the National Geographic Society's explorations, suggest that the Bonitians were subjected to a constantly increasing pressure from nomadic tribes and that the village folk were prompted, from time to time, to increase the impregnability of their communal home. Sporadic warfare, together with altered agricultural conditions, may well have forced the abandonment of Pueblo Bonito approximately one thousand years ago.